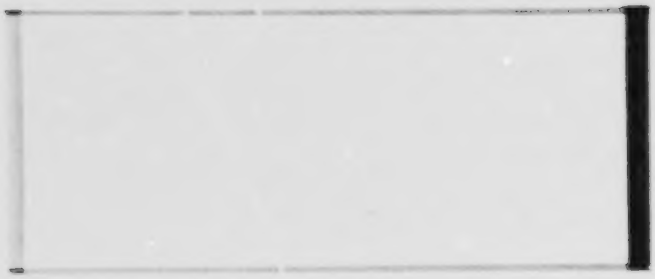


rpc

RESEARCH AND PRODUCTIVITY COUNCIL

LE CONSEIL DE RECHERCHE ET DE PRODUCTIVITE

RESEARCH AND PRODUCTIVITY COUNCIL
College Hill Road
P.O. Box 6000
Fredericton, N.B.
E3B 5H1
Telephone 506-452-8994 Telex 014-46115 Fax 506-452-1395

MODIFICATIONS OF EXISTING TESTING FACILITIES, OPTIMIZATION OF HYDRORETORTING CONDITIONS AND ASSESSMENT OF CANADIAN OIL SHALES AS SOURCE OF SYNTHETIC FUELS

Final Report

by

Mineral Development and Processing
The Research and Productivity Council

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS FILE NUMBER	:	18SQ.23440-2-9015
DSS CONTRACT SERIAL NUMBER	:	OSQ82-00053
CANMET PROJECT NUMBER	:	420301
CANMET SCIENTIFIC AUTHORITY	:	Mr. E. Furimsky

140 pp

JN:8920
March 30, 1983
Report Number MDP/83/12

MICROMEDIA

TABLE OF CONTENTS

		Page
1.0	SUMMARY	1
2.0	RECOMMENDATIONS	3
3.0	INTRODUCTION	6
	3.1 General	7
	3.2 Contract Objectives	7
	3.2.1 Modification of Existing Facility	8
	3.2.2 Optimization of Hydroretorting Conditions	8
	3.2.3 Evaluation of Oil Shales from Different Provinces	8
	3.2.4 Evaluation of Oil Shales from New Brunswick	9
4.0	EXPERIMENTAL	10
	4.1 Modification of Hydroretorting Apparatus	10
	4.2 Testing of Hydroretorting Apparatus	10
	4.3 Optimization of Hydroretorting Conditions	16
	4.4 Hydroretorting	16
	4.5 Sample Selection	19
5.0	RESULTS	20
6.0	DISCUSSIONS AND CONCLUSIONS	37
7.0	ACKNOWLEDGEMENTS	44
8.0	REFERENCES	46
9.0	APPENDICES	48
	9.1 Statement of Work	49
	9.2 Sample Details	52
	9.3 IGT Report	77
	9.4 Gas Chromatograms of Liquid Products	86
	9.5 Gas Chromatograms of Effluent Gasses	127

LIST OF TABLES

TABLE		Page
1	OPTIMIZATION OF HYDRORETORTING CONDITIONS	17
2	PROXIMATE ANALYSIS OF RAW OIL SHALES	23
3	COMPOSITION OF RAW OIL SHALES	25
4	MAJOR ELEMENT COMPOSITION OF RAW OIL SHALES	27
5	FISCHER ASSAY OF OIL SHALES	29
6	HYDROGEN RETORT OF OIL SHALES	31
7	COMPOSITION OF SPENT OIL SHALES	33
8	COMPOSITION OF SELECTED SHALE OILS FROM HYDROGEN RETORTING TESTS	35
9	NITROGEN RETORT OF SELECTED OIL SHALES	36
10	COMPARISON OF IGT AND RPC HYDROGEN RETORTING OF KENTUCKY OIL SHALE	38
11	CARBON CONVERSION RATES AND OIL YIELDS OF OIL SHALES RETORTED AT 500 PSI HYDROGEN AND NITROGEN	43

LIST OF FIGURES

FIGURE		
1	SCHEMATIC OF HYDRORETORT APPARATUS	13
2	PHOTOGRAPH OF HYDRORETORT FACILITY	14
3	PHOTOGRAPH OF PREHEATER AND SAMPLE CHAMBER	14
4	PHOTOGRAPH OF CONDENSATE COLLECTION SYSTEM	15
5	PHOTOGRAPH OF SHALE OIL COLLECTED IN COLLECTION VESSEL	15
6	EFFECTS OF HYDROGEN PARTIAL PRESSURE ON OIL YIELD AND TOTAL YIELD	40
7	EFFECTS OF HYDRORETORTING TEMPERATURE ON OIL YIELD AND TOTAL YIELD	40
8	RELATIONSHIP OF HYDROGEN PARTIAL PRESSURE AND CARBON CONVERSION FOR EASTERN AND WESTERN UNITED STATES OIL SHALES	41

1.0 SUMMARY

1.0 SUMMARY

A test facility previously developed at RPC for retorting oil shales under hydrogen pressures was modified to improve oil recoveries. The hydroretorting conditions were optimized at 500 psi hydrogen, 700°C, and 8°C/min heat-up rate using a Kentucky oil shale sample previously evaluated at the Institute of Gas Technology, Chicago, Illinois. Oil quantities recovered from the RPC facility were comparable to results from IGT.

The optimized conditions for the Kentucky oil shale were used to evaluate a total of 37 oil shale samples from New Brunswick, Ontario, Nova Scotia, Newfoundland, British Columbia, and Quebec. Hydrogen retorting increased the oil yields from 6 percent to greater than 150 percent over Fischer assay. Organic conversion rates were also increased under hydrogen retorting for all shale samples tested.

The highest grades of oil shale tested were from Albert county, New Brunswick. The average oil yields for five New Brunswick samples increased from 20.0 gal/ton for nitrogen retorting to 38.4 gal/ton for hydroretorting.

2.0 RECOMMENDATIONS

2.0 RECOMMENDATIONS

2.1 Modifications to the Hydroretort Apparatus

Although the modified hydroretort rig proved acceptable for accomplishing the tasks defined in the work statement of this study, several further refinements are recommended to improve control of operational parameters and to increase sample throughput in future programs. These include: the addition of programmable temperature controllers to improve the control of heat-up rate; the use of a data acquisition system to reduce manpower requirements; and the incorporation of the oven-heating elements into a hinged oven structure to reduce assembly and reassembly time.

2.2 Further Evaluation of New Brunswick Oil Shales

Since the New Brunswick oil shales appear to exist with the greatest reserves at the highest oil grades and exhibited favourable response to hydroretorting, it is recommended that a detailed study be performed on samples selected from this reserve. The study presented in this report used a common set of hydroretorting test conditions determined from the optimization of oil yields from a standard Kentucky oil shale. Since the objective of the study was to survey Canadian shales with respect to potential for hydroretort processing, the conditions which produced the maximum hydrocarbon recovery and, in particular, liquid oil yields from the Kentucky sample were employed for all Canadian samples, regardless of economic considerations.

The detailed study of New Brunswick shales would consist of two phases.

The first phase would consist of a study of the response of New Brunswick shales to changes in the hydroretorting conditions; namely hydrogen pressure, hydrogen flow rate, final temperature, heat-up rate, and particle size. The Institute of Gas Technology[1] (IGT) has shown that shale from different formations, even within the same reserve, may respond quite differently to hydroretorting. For example,

pressure and temperature conditions required for maximum liquid oil yields have been shown to vary significantly throughout a reserve. Similar effects have been noted for hydrogen consumption, gas yields, and oil and gas characteristics which are important to refining considerations. Information on the effects of hydroretorting conditions on oil and gas yields is the necessary first step for an economic evaluation of the process on the New Brunswick reserves.

The second phase of the recommended study is a comparative evaluation of hydroretorting and conventional retorting technologies as applied to New Brunswick reserves. This would include compilation and study of reserve data and existing core samples, collection and selection of samples from different stratigraphic units representative of the oil shale reserves, testing of samples for Fischer retort and hydroretort response, and preliminary feasibility studies of hydroretorting processing of New Brunswick oil shales.

2.3 Flash Retorting of New Brunswick Oil Shales

It is recommended that the response of the New Brunswick oil shales to flash pyrolysis be examined. This study could begin with a simple program using a pyroprobe-G.C. and/or a flash pyrolysis apparatus such as the RPC-AECL hydropyrolysis test rig. This rig is capable of operating at 700°C and up to 500 psi with semicontinuous flash injection of sample. Follow-up programs would involve fluidized bed and/or Vortactor mini-pilot test runs. It is recommended that both hydrogen and nitrogen carrier gases and atmospheric and pressure conditions be examined.

3.0 INTRODUCTION

3.0 INTRODUCTION

3.1 General

Many oil shales are considered unsatisfactory feed stocks because of their low oil yields in the Fischer assay test and in conventional thermal retorting. When conventional retorting processes are applied to hydrogen deficient oil shales such as eastern United States oil shales, a large fraction of the organic carbon remains as coke. The Institute of Gas Technology (IGT) has shown that hydrogen retorting at elevated pressures enhances the yields of shale oils and hydrocarbon gasses obtained by retorting.[1] Their results showed that hydroretorting increased organic carbon conversions 20 percent for western United States oil shales (78 to 95 percent) and 150 percent (35 to 90 percent) for eastern United States oil shales.

Under a previous CANMET contract[2], the Applied Science and Technology Department of RPC developed a hydrogen retort facility for testing the retorting behaviour of oil shales. The RPC hydrogen retort facility was used to test six oil shale samples from New Brunswick in the original program. The hydrogen retort tests gave carbon conversion rates of 53 to 87 percent which were comparable to that for the Fischer retorting. Retorting at 500°C gave oil yields similar to the Fischer assay, and at 700°C oil yields were reduced. Hence, in the retorting tests the use of hydrogen at 500 psi did not appear to increase yields. Since only six tests were performed in this study and oil mist escapement was observed in all these tests resulting in poor mass balances, it was decided that further work was required in a test unit modified for superior oil capture.

3.2 Contract Objectives

This work is a continuation of the first contract; "Construction of a Test Facility and Hydroretorting of Oil Shales from New Brunswick."[2] There were four parts to the present program conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada (Appendix 1).

3.2.1 Modification of Existing Facilities

Several modifications to the existing hydroretorting apparatus were to be made prior to testing of oil shales. These included shortening the exit tubing between the retort and the collection vessel and controlling the temperature of the exit line at approximately 200°C.

3.2.2 Optimization of Hydroretorting Conditions

The hydroretorting conditions were to be optimized with respect to hydrocarbon recovery and, in particular, liquid oil yields, using a standard Kentucky oil shale sample. The optimization study was to include the following parameters:

a) Hydroretorting at 500°C, 550°C, 620°C, and 700°C.
b) Hydroretorting at 100, 300, and 500 psig. hydrogen.
c) Hydroretorting with three particle sizes.
d) Hydroretorting with different amounts of sample.

For comparison purposes, arrangements were made to have an exactly equivalent sample evaluated at the Institute of Gas Technology, Chicago.

3.2.3 Evaluation of Oil Shales from Different Provinces

Samples from Ontario, Quebec, Nova Scotia, and Newfoundland were to be evaluated using the conditions established during the optimization study. The characterization of the materials were to include:

Raw shale - mineral carbon, organic carbon, hydrogen, oxygen, nitrogen, sulphur, moisture, volatiles at 950°C, ash, major elements, calorific value, and Fischer assay.

Spent shale - mineral carbon, organic carbon, hydrogen, oxygen, nitrogen, sulphur, and calorific value.

Liquid products - gas chromatography finger printing, carbon, oxygen, nitrogen, sulphur, specific gravity, and calorific value.

Gas products - gas chromatography during run.

3.2.4 Evaluation of Oil Shales from New Brunswick

Oil shale samples from New Brunswick were to be evaluated with the hydroretort apparatus. The raw shales, spent shales, and products were to be characterized as outlined in the preceding section. Samples that gave high liquid yields were to be retorted in the same apparatus with nitrogen for comparison.

4.0 EXPERIMENTAL

4.0 EXPERIMENTAL

4.1 Modifications of Hydroretorting Apparatus

Several modifications to the existing hydroretorting apparatus were made to ensure safe operating conditions during the high temperature and pressure testing. The complete apparatus was mounted on a two inch steel frame with a 3/16 inch steel plate shielding the operator from the high temperature and pressure portion of the equipment. A pressure gauge and safety relief valve were added to the gas line to help monitor the pressure and prevent the maximum limit from being exceeded.

Additional modifications were made to maximize the collection of products in the retorting tests. The exit line between the retort and the pressure reducing valve was shortened. The exit line and valve were wrapped with heating tape to control the temperature and eliminate the condensation of products in the line. Also, a thermocouple was placed in the exit gas stream to monitor the temperature during tests.

The condensing and collection system was improved from the earlier design. The line between the high pressure valve and the collection tube was shortened and the "rubber stopper" connectors were replaced by ball and socket glass joints with teflon gaskets.

The samox heating tapes used to heat the preheater and sample tube were replaced with oven heating coils. These coils reduced the possibility of electrical shorting between the heaters and reactor and could be operated safely to 850°C.

4.2 Testing of Hydroretorting Apparatus

The existing hydroretorting equipment and modifications were evaluated and tested using nitrogen gas. A total of six tests were run at the following range of conditions:

Pressure	- 500 psi nitrogen
Gas Flow	- 150 ml/minute to 500 ml/minute
Maximum Temperature	- 500°C and 700°C
Heating Rate	- 4°C/minute to 8°C/minute
Sample	- approximate 75 grams Kentucky oil shale

There were several problems encountered in the initial tests. The problems and remedies were as follows:

a) Oil fumes were observed escaping from the exit of the water condenser. The water condenser was removed and replaced with a liquid nitrogen trap.

b) It was difficult to heat up the system at a faster rate than 5°C per minute. A second preheater consisting of 3/8 inch tube coiled around the original preheater was added to the system.

c) The temperature of the oil shale and gas were inconsistent. The thermocouples in the original apparatus were found to be mounted on the walls of the preheater and sample holder. Additional thermocouples were added to the system; one in the gas stream at the exit of the preheater and one ir the oil shale sample. These temperatures were then used to control the heating rate.

d) The temperature was difficult to control during the heating up of the apparatus at specific rates. Several of the coils were placed in series for easier controlling and the operators were given additional training.

The final modified apparatus is shown in Figures 1 to 5. The equipment operated successfully during the retorting and hydroretorting tests. The sample chamber had to be replaced once during the testing due to a leaking flange and one heating coil was replaced. Difficulties were experienced during manual heating of the apparatus at the given rates. Practice and experience by the technicians helped to minimize the problem.

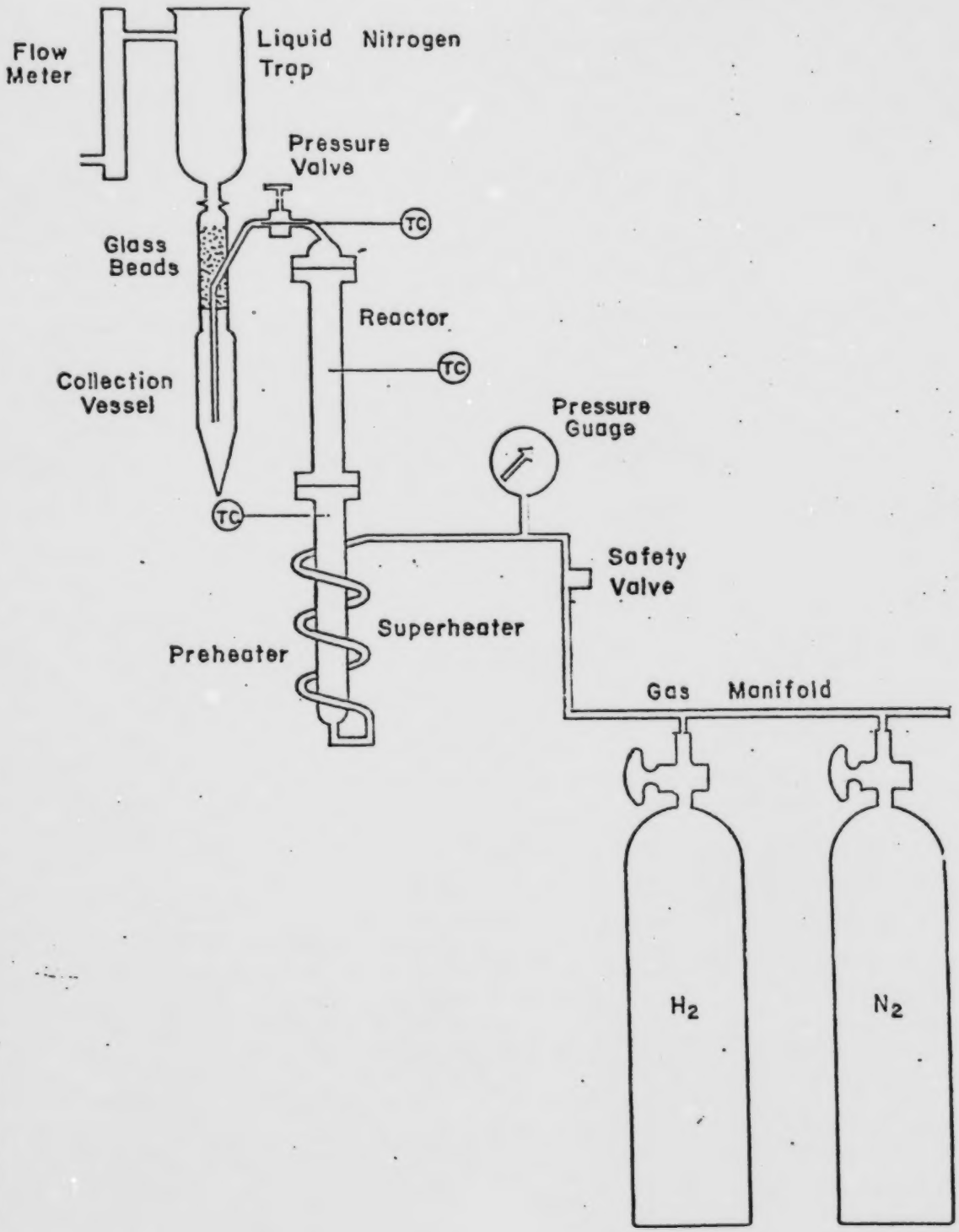


FIGURE 1. HYDRORETORT APPARATUS

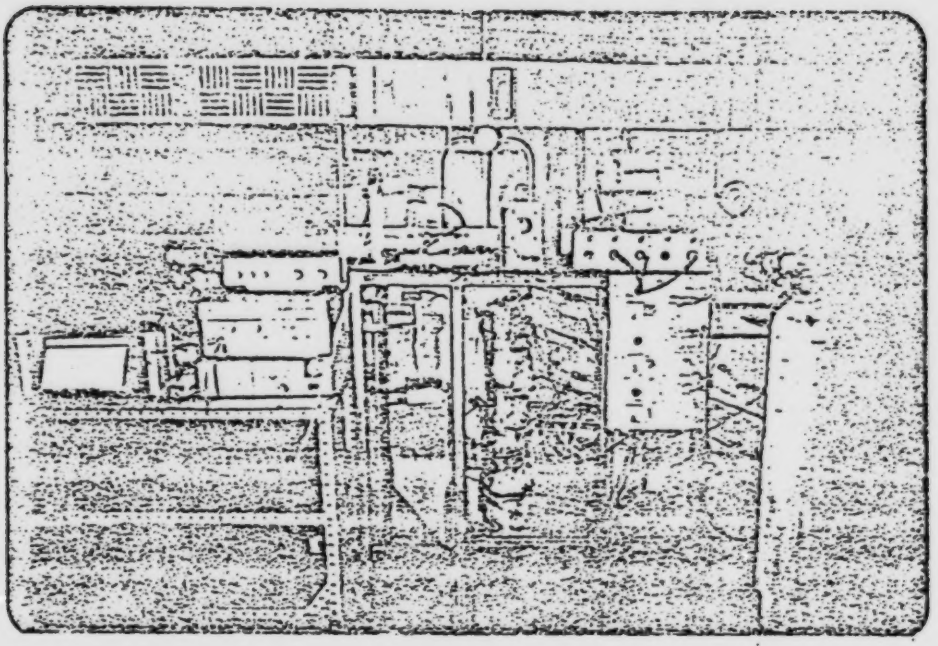


FIGURE 2 PHOTOGRAPH OF HYDRORETORT FACILITY

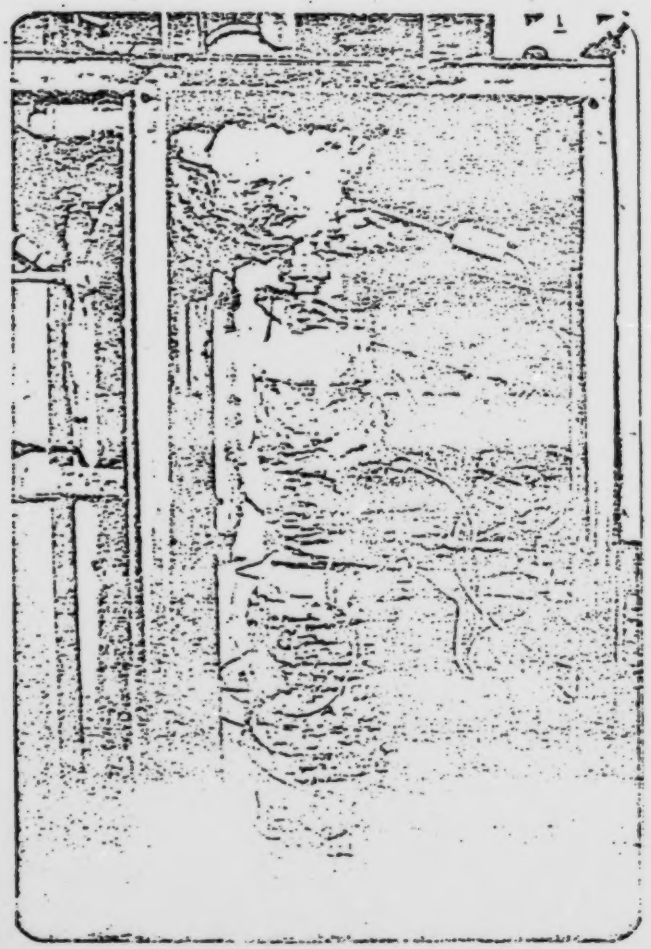


FIGURE 3 PHOTOGRAPH OF PREHEATER AND SAMPLE CHAMBER

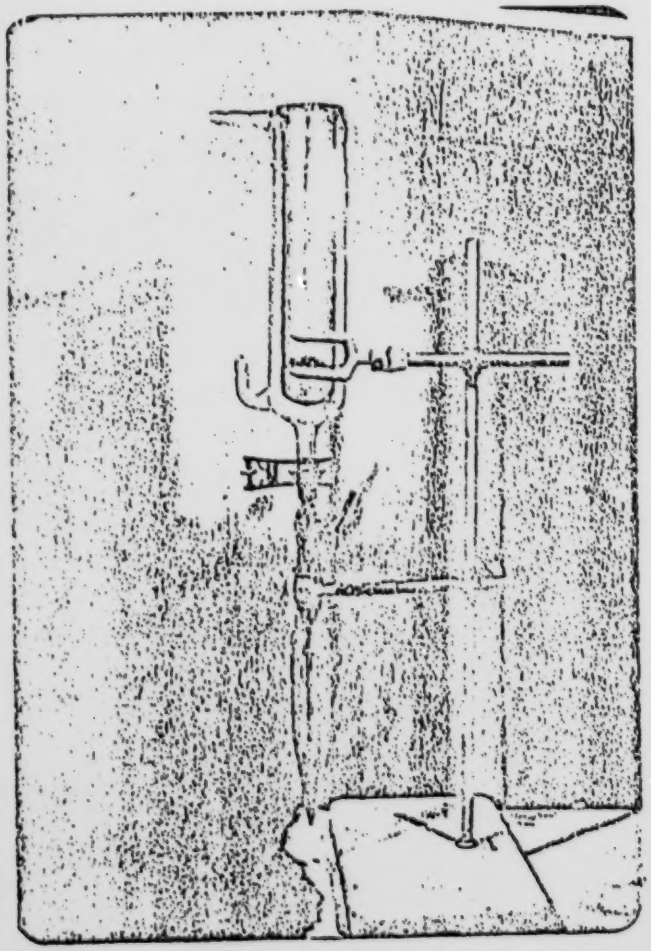


FIGURE 4 PHOTOGRAPH OF CONDENSATE COLLECTION SYSTEM

FIGURE 5 PHOTOGRAPH OF SHALE OIL COLLECTED IN COLLECTION VESSEL

4.3 Optimization of Hydroretorting Conditions

A total of fourteen runs were made during the optimization phase of the contract. An oil shale sample from the Institute for Mining and Minerals Research, University of Kentucky, was used for all optimization tests (Appendix 2). A sample of the oil shale was sent to the Institute of Gas Technology, ITT Centre, Chicago, Illinois for hydroretorting testing and comparison. A copy of the report is included in Appendix 3.

The results of the optimization tests are given in Table I. From the results it was determined that the maximum pressure of 500 psi H_2 and the high temperature of 700°C gave the highest liquid yields. A smaller sample size and a mesh size down to +18 had little effect on the yields. A sample size smaller than 18 mesh decreased the liquid yield as did a heating rate of over 10° per minute.

The retorting conditions selected for the evaluation of the oil shales were as follows:

Pressure	:	500 psi H_2
Temperature	:	700°C
Heating Rate	:	8°C per minute
Sample Size	:	40 gm to 75 gm
Mesh Size	:	-6+18 (U.S. standard size)
Gas Flow	:	500 ml per minute

4.4 Hydroretorting

Based on the preliminary testing, the following procedure was developed for the hydroretorting tests:

a) The sample of oil shale was crushed and screened to a mesh size of -6+18.

b) Approximately 75 grams of the sample were weighed and placed in an oven at 100°C for 12 hours, and 40 grams were ground and saved for analysis.

TABLE 1

OPTIMISATION OF HYDRORETORTING CONDITIONS

Test #	Gas Pressure (psi)	Temperature Final (°C)	Temperature Rate (°C/min)	Sample wt (gm)	Sample Size (mesh)	H_2O (wt %)	Gas & Losses (wt %)	Oil (wt %)
8	H_2 - 500	500	8/min	75.12	-6+10	3.1	2.7	7.1
9	H_2 - 500	600	8/min	75.05	-6+10	3.5	3.5	7.2
10	H_2 - 500	700	8/min	75.06	-6+10	4.3	4.0	7.5
11	H_2 - 300	700	8/min	75.06	-6+10	4.5	4.8	6.7
12	H_2 - 100	700	8/min	75.04	-6+10	4.4	2.4	6.7
13	H_2 - 100	600	8/min	75.02	-6+10	4.2	3.1	5.4
14	H_2 - 500	700	8/min	37.54	-6+10	4.4	3.9	7.5
15	H_2 - 500	700	8/min	75.07	-14+18	4.4	4.1	7.5
16	H_2 - 500	700	8/min	75.07	-18	4.4	3.5	7.1
17	H_2 - 500	700	10/min	75.02	-6+10	4.9	3.5	7.2
18	H_2 - 300	700	8/min	75.04	-6+10	4.6	2.8	7.3
19	H_2 - 300	700	8/min	75.07	-6+10	4.8	3.4	6.7
20	H_2 - 500	700	8/min	75.50	-6+10	4.6	3.9	7.3
21	H_2 - 500	700	12/min	74.99	-6+10	4.0	4.0	6.7

c) The dried sample was weighed and placed in the retort sample chamber.

d) The collection vessel and liquid nitrogen trap were cleaned, weighed, and assembled.

e) The retorting tests were run using the conditions determined during the optimization tests. The exit line temperature was maintained at approximately 400°C and the temperature of the retort was held at the maximum for fifteen minutes before shutdown.

f) The retort was disassembled and the weights of the spent shale, collection vessel, and liquid nitrogen trap were recorded. The oil sample was centrifuged and the millilitres of water were recorded.

The characterization of the oil shales and products included the following:

Raw Shale - Moisture, ash, volatile matter at 950°C, fixed carbon, mineral carbon, organic carbon, hydrogen, nitrogen, sulphur, oxygen, calorific value, major elements, and Fischer assay.

Spent Shale - Mineral carbon, organic carbon, hydrogen, nitrogen, sulphur, oxygen, calorific value.

Liquid Products - Carbon, hydrogen, nitrogen, sulphur, oxygen, specific gravity, calorific value, chromatography finger printing.

Gasses - One sample was taken and analysed immediately at the end of heat-up (700°C) in each hydroretorting test.

A number of samples were retorted with nitrogen instead of hydrogen for comparison purposes. The same conditions and procedures were followed except nitrogen was substituted for hydrogen.

4.5 Sample Selection

Arrangements were made for the procurement of samples from the oil shale formations selected by the contracts Scientific Authority. It was the purpose of the program to establish the response of a wide variety of Canadian oil shales to hydroretorting. Regional geologists randomly selected samples from the deposits based on their general knowledge of the areas and the availability of the samples.

5.0 RESULTS

5.0 RESULTS

A total of 37 oil shale samples were evaluated using the hydroretorting facility described in the experimental section. These samples included 17 from New Brunswick, 5 from Ontario, 2 from Nova Scotia, 2 from Newfoundland, 1 from British Columbia, 9 from Quebec, and 1 from Kentucky. Further details of the samples are given in Appendix 2.

The proximate analyses of the raw oil shales are in Table 2. The ultimate analyses of the shales follow in Table 3 and the major element compositions in Table 4.

Fischer assays were run at RPC according to the United States Bureau of Mines procedure.[3] The results of the Fischer retorting of the 37 samples are given in Table 5.

The results of the hydrogen retorting tests are given in Table 6. The spent shales from the hydroretorts were analysed for mineral carbon, organic carbon, hydrogen, nitrogen, sulphur, oxygen, and calorific value. These results are reported in Table 7. Liquid products from the retorts were analysed by capillary gas chromatography. Chromatography traces can be found in Appendix 4. All oil samples of sufficient quantity for chemical analysis were tested for carbon, hydrogen, nitrogen, sulphur, oxygen, and calorific value and the results are recorded in Table 8.

A number of the oil shale samples that gave high yields of liquid during hydroretorting compared to that from the Fischer assays were retorted in the hydroretort facility using nitrogen. All experimental conditions were duplicated except 500 psi of nitrogen was substituted for 500 psi hydrogen. These tests are reported in Table 9.

Sample chromatograms of the effluent gases are shown in Appendix 5. The gases consisted of oxygen, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, propane, and carrier gas. Generally the concentration of the gaseous hydrocarbons increased as the organic carbon conversion rate increased (methane > ethane > propane).

Since the composition of the off gasses changes with time during a retorting test, the one GC sample taken in each test was not necessarily representative of the composition of the total gas generated during the test. Therefore the gas data could only be used as a semi-quantitative result for comparative purposes. It is recommended in future, more detailed studies that the total off gas generated in a test be collected in a large sample bag or balloon. GC's of samples taken from this balloon would result in a quantitative result for the entire hydro-retorting run.

TABLE 2

PROXIMATE ANALYSIS OF RAW OIL SHALES

Sample	Moisture (wt %)	Ash (wt %)	Volatile Matter (wt %)	Fixed Carbon (wt %)
NB-1	0.76	72.20	26.52	1.52
NB-2a	1.28	75.48	19.97	3.27
NB-2b	3.84	86.56	10.50	<0.10
NB-3	0.95	76.72	20.62	1.71
NB-4	1.48	71.03	26.10	1.39
NB-5	1.23	72.78	22.39	3.60
NB-6	0.66	69.58	27.91	1.85
NB-7	0.53	58.99	40.89	<0.10
NB-8	0.61	66.52	30.31	2.56
NB-9	0.80	75.01	22.22	1.97
NB-10	0.35	79.04	18.15	2.46
NB-11	0.66	75.41	24.17	<0.10
NB-12	0.46	79.30	20.44	<0.10
NB-13	0.41	80.16	19.05	0.38
NB-14	0.19	80.46	17.11	2.43
NB-15	0.30	87.64	11.58	0.48
NB-16	0.53	60.05	38.58	0.84
ONT-1199	0.66	82.34	14.97	2.03
ONT-1200	0.46	70.61	27.22	1.71
ONT-1201	0.88	87.02	9.28	2.82

TABLE 2 CONTINUED

Sample	Moisture (wt %)	Ash (wt %)	Volatile Matter (wt %)	Fixed Carbon (wt %)
ONT-55	0.28	73.20	31.74	<0.01
ONT-C7A	0.28	68.04	28.24	3.44
NS-SP1	2.54	79.06	18.50	<0.01
NS-SP2	1.61	82.02	14.58	1.79
NFLD-189-6	0.83	75.23	21.92	2.02
NFLD-189-10	0.60	73.24	23.35	2.81
BC-1	0.53	86.02	12.32	1.13
QUE-1	1.38	71.83	25.48	1.31
QUE-2	0.50	67.91	28.87	2.72
QUE-3	0.63	69.24	27.23	2.90
QUE-4	1.15	91.08	5.05	2.72
QUE-5	1.00	89.84	7.77	1.39
QUE-6	0.90	94.50	3.64	0.96
QUE-7	0.81	93.05	5.28	0.86
QUE-8	1.09	86.51	11.44	0.96
QUE-9	0.59	77.06	22.14	0.21
KT	0.87	84.61	12.88	1.64

TABLE 3

COMPOSITION OF RAW OIL SHALES
(wt % - dry basis)

Samples	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	BTU/lb
NB-1	3.65	10.88	1.61	0.14	0.52	12.23	2220
NB-2a	1.33	13.57	2.23	0.17	0.25	7.29	2528
NB-2b	0.85	3.48	1.30	0.04	0.29	8.01	680
NB-3	1.02	12.15	1.88	0.12	0.12	8.20	2365
NB-4	1.89	13.20	2.21	0.13	0.15	11.82	2514
NB-5	5.78	10.83	2.43	0.17	0.19	8.14	2994
NB-6	6.41	7.65	1.49	0.06	<0.01	15.01	1676
NB-7	6.12	12.62	2.65	0.07	<0.01	20.20	2500
NB-8	7.65	4.73	0.90	0.04	0.08	20.31	635
NB-9	2.59	14.52	2.32	0.17	<0.01	5.59	2948
NB-10	1.28	7.78	0.83	0.04	0.04	11.06	1000
NB-11	1.73	17.01	2.20	0.24	1.44	2.12	3701
NB-12	1.10	12.66	1.46	0.11	0.76	4.70	2323
NB-13	2.83	8.18	1.18	0.03	0.56	7.13	1676
NB-14	4.60	4.13	0.71	0.03	0.95	9.16	889
NB-15	3.35	1.22	0.30	0.06	0.86	6.60	287
NB-16	3.01	25.33	3.35	0.45	0.48	7.53	5320
ONT-1199	1.52	9.85	1.35	0.19	1.78	3.99	1882
ONT-1200	3.28	8.89	1.00	0.31	1.24	14.81	1398

TABLE 3 CONTINUED

Samples	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	BTU/lb
ONT-1201	2.05	6.13	1.07	0.16	1.31	2.37	1305
ONT-55	4.18	5.85	0.81	0.15	1.47	10.62	1181
ONT-C7A	2.48	6.45	0.80	0.22	0.96	16.96	1165
NS-SP1	0.57	11.39	1.84	0.39	0.58	6.71	1792
NS-SP2	0.80	8.38	1.31	0.25	0.56	6.96	1238
NFLD-189-6	3.90	3.90	0.76	0.09	0.10	16.16	572
NFLD-189-10	4.30	5.30	0.85	0.06	0.13	16.12	706
BC-1	2.38	6.18	0.70	0.15	0.85	3.72	1234
QUE-1	4.33	1.12	0.53	0.09	0.30	22.20	≠
QUE-2	7.57	1.23	0.56	0.06	0.45	22.38	227
QUE-3	7.50	1.11	0.20	0.08	0.46	21.61	≠
QUE-4	1.39	1.73	0.66	0.11	1.35	3.68	229
QUE-5	1.22	1.55	0.58	0.12	1.27	5.42	259
QUE-6	0.63	1.10	0.56	0.10	1.05	2.06	42
QUE-7	0.35	1.13	0.58	0.07	1.25	3.57	188
QUE-8	2.14	1.05	0.64	0.07	1.17	8.42	115
QUE-9	4.58	1.23	0.50	0.06	0.70	15.87	63
KT	0.0	11.65	1.48	0.28	2.02	0.31	2097

≠ BTU/lb determined to be zero

TABLE 4

MAJOR ELEMENT COMPOSITIONS OF RAW SHALES

Sample	SiO_2 (wt %)	Al_2O_3 (wt %)	Fe_2O_3 (wt %)	CaO (wt %)	MgO (wt %)	Na_2O (wt %)	K_2O (wt %)
NB-1	33.88	8.83	4.33	12.40	4.31	1.91	2.04
NB-2a	43.48	17.33	5.13	5.06	1.95	2.02	2.08
NB-2b	46.91	23.23	7.32	2.56	2.36	1.71	3.08
NB-3	48.72	9.40	4.60	6.15	2.16	0.74	0.60
NB-4	38.14	7.27	4.16	12.20	1.31	1.43	1.37
NB-5	38.27	18.85	4.45	7.37	1.63	1.35	1.56
NB-6	25.83	12.54	3.24	23.15	1.18	3.16	1.66
NB-7	16.95	13.47	2.75	14.54	11.01	1.00	0.55
NB-8	22.08	8.25	7.63	16.48	10.14	1.39	0.82
NB-9	41.05	15.28	6.69	4.85	1.82	1.57	2.06
NB-10	40.11	12.90	7.78	9.63	5.20	3.09	1.83
NB-11	39.28	18.19	5.93	3.97	1.69	4.93	1.56
NB-12	39.72	21.24	5.92	4.93	2.43	4.43	2.24
NB-13	40.36	15.90	8.02	6.80	3.61	4.13	2.11
NB-14	39.40	14.53	6.32	10.90	4.77	3.88	2.04
NB-15	43.71	21.17	6.29	7.34	2.64	5.16	3.18
NB-16	27.93	15.54	4.67	5.82	2.51	3.25	1.60
ONT-1199	46.01	19.86	5.65	5.07	2.32	0.77	3.77
ONT-1200	27.53	11.53	3.79	15.46	5.69	0.68	2.90
ONT-1201	57.17	16.47	6.39	1.92	1.69	1.14	3.46

TABLE 4 CONTINUED

Sample	SiO_2 (wt %)	Al_2O_3 (wt %)	Fe_2O_3 (wt %)	CaO (wt %)	MgO (wt %)	Na_2O (wt %)	K_2O (wt %)
ONT-55	28.79	3.72	4.49	14.75	5.77	0.92	2.96
ONT-C7A	21.34	7.02	2.65	24.37	1.80	0.99	1.56
NS-SP1	46.76	19.39	8.25	1.73	1.02	0.50	0.97
NS-SP2	48.06	17.87	6.68	4.42	1.36	0.74	1.95
NFLD-189-6	38.53	6.72	5.91	11.98	10.60	1.32	1.23
NFLD-189-10	33.43	10.41	3.38	12.22	10.44	1.00	0.97
BC-1	49.19	20.48	2.78	6.05	5.69	0.72	0.03
QUE-1	24.02	12.00	2.05	21.41	1.19	1.16	1.98
QUE-2	20.78	7.03	1.70	28.13	1.77	1.42	1.53
QUE-3	16.79	5.77	2.14	23.27	1.63	0.84	1.02
QUE-4	54.45	19.86	6.12	3.41	2.57	1.17	3.71
QUE-5	52.71	17.29	6.84	5.52	3.20	2.52	3.58
QUE-6	57.10	21.97	7.05	2.06	3.21	1.80	3.85
QUE-7	52.28	21.19	5.98	6.44	3.41	1.15	3.56
QUE-8	46.37	17.16	5.74	8.06	3.11	1.18	2.61
QUE-9	34.82	12.41	3.06	25.11	2.41	1.05	1.72
KT	47.36	27.58	5.75	0.19	1.45	0.66	3.55

TABLE 5

FISCHER ASSAY OF OIL SHALES

Sample	Water wt %	Gas & Loss wt %	Oil wt %	Density g/ml(15.5°C)	Oil* gal/ton
NB-1	2.9	0.3	7.8	0.8909	17.4
NB-2a	1.8	4.4	7.8	0.8883	17.4
NB-2b	6.5	0.9	1.6	------	3.6
NB-3	2.4	2.4	7.7	0.8799	17.2
NB-4	3.5	3.1	8.9	0.8807	19.9
NB-5	2.9	4.0	9.1	0.8833	20.4
NB-6	1.1	2.3	5.6	0.8832	12.5
NB-7	0.7	2.0	10.3	0.8755	23.0
NB-8	1.3	0.9	3.3	------	7.4
NB-9	2.5	3.7	9.6	0.9014	21.5
NB-10	0.4	1.8	3.3	------	7.4
NB-11	0.9	2.6	12.5	0.8942	22.0
NB-12	0.6	2.3	7.6	0.8911	17.0
NB-13	1.3	1.4	5.3	0.9029	11.9
NB-14	0.4	1.2	2.9	------	6.5
NB-15	0.3	0.8	0.4	------	0.9
NB-16	1.5	4.1	19.4	0.9335	43.4
ONT-1199	0.7	2.5	4.8	------	10.7
ONT-1200	0.5	1.9	3.0	------	6.7
ONT-1201	1.1	2.9	2.0	------	4.5
ONT-55	0.4	2.2	3.2	------	7.2

TABLE 5 CONTINUED

Sample	Water wt %	Gas & Loss wt %	Oil wt %	Density g/ml(15.5°C)	Oil* gal/ton
ONT-C7A	0.6	2.6	3.2	------	7.2
NS-SP1	5.3	2.4	1.8	------	4.0
NS-SP2	2.8	1.7	2.5	------	5.6
NFLD-189-6	1.1	1.8	2.6	------	5.8
NFLD-189-10	0.7	1.7	3.6	------	8.0
BC-1	0.4	1.9	2.0	------	4.5
QUE-1	1.1	1.7	0.0	------	0.0
QUE-2	0.6	0.6	0.3	------	0.7
QUE-3	0.9	1.0	0.1	------	0.2
QUE-4	1.0	0.8	0.2	------	0.4
QUE-5	0.9	0.3	0.0	------	0.0
QUE-6	0.8	0.2	0.1	------	0.2
QUE-7	1.0	0.4	0.1	------	0.2
QUE-8	0.9	0.4	0.2	------	0.4
QUE-9	1.5	0.4	0.1	------	0.2
KT	2.8	2.6	4.2	0.9360	9.2

*Based on average density of oils at 15.5°C of 0.8921.

------ insufficient sample to determine density

TABLE 6

HYDROGEN RETORT OF OIL SHALES**

Samples	Moisture wt %	Water wt %	Gas & Loss wt %	Oil Wt %	Density g/ml (15.5°C)	Oil* gal/ton
NB-1	1.0	5.1	6.1	11.2	0.8706	25.6
NB-2a	2.8	6.8	10.7	14.4	0.8699	32.9
NB-2b	6.8	10.3	0	3.9	------	7.3
NB-3	1.1	6.0	3.6	11.7	0.8755	26.8
NB-4	2.6	6.7	2.1	12.0	0.8557	27.4
NB-5	1.9	6.4	0.6	15.4	0.8513	35.2
NB-6	0.9	3.6	3.3	9.0	0.8979	20.6
NB-7	0.4	5.5	17.5	10.7	0.8688	24.5
NB-8	0.2	2.8	14.9	6.8	0.8582	15.6
NB-9	0.7	5.5	3.7	14.1	0.8643	32.2
NB-10	0.2	5.1	7.6	7.2	------	16.5
NB-11	0.3	2.6	9.9	20.0	0.8789	45.7
NB-12	0.4	2.6	6.2	12.2	0.8988	27.9
NB-13	0.4	4.4	5.8	11.1	0.9006	25.4
NB-14	0.1	2.6	7.7	5.8	------	13.3
NB-15	0.1	2.1	12.4	2.3	------	5.3
NB-16	0.4	4.8	12.4	20.2	0.8431	46.2
ONT-1199	0.6	3.9	4.3	7.1	------	16.2
ONT-1200	0.6	2.6	7.7	5.2	------	11.9
ONT-1201	1.0	2.5	2.3	6.7	------	15.3
ONT-55	0.5	4.9	8.4	6.4	------	14.6

TABLE 6 CONTINUED

Samples	Moisture wt %	Water wt %	Gas & Loss wt %	Oil Wt %	Density g/ml (15.5°C)	Oil* gal/ton
ONT-C7A	0.6	2.6	6.4	4.5	------	10.3
NS-SP1	4.2	7.8	29.5	5.7	------	13.0
NS-SP2	2.3	6.8	4.5	3.7	------	8.5
NFLD-189-6	0.8	3.2	7.6	5.3	------	12.1
NFLD-189-10	0.5	3.3	10.1	5.3	------	12.1
BC-1	0.4	3.1	4.5	4.9	------	11.2
QUE-1	1.3	5.3	4.8	1.7	------	3.9
QUE-2	0.5	3.0	1.4	4.0*	------	9.1
QUE-3	0.5	3.2	4.1	1.6	------	3.6
QUE-4	1.3	4.5	2.6	1.5	------	3.4
QUE-5	1.0	4.8	3.8	0.6	------	1.4
QUE-6	1.1	3.2	0.0	1.7	------	3.9
QUE-7	1.1	3.5	1.2	1.5	------	3.4
QUE-8	1.4	4.9	8.9	2.3	------	5.2
QUE-9	0.2	1.6	0	0.1	------	0.2
KT	2.1	4.4	4.0	7.45	0.9326	15.8

* Based on density of oils 0.8726

** wt % calculated for oil shale as received basis (water wt % includes moisture)

------ insufficient sample to determine density

TABLE 7

COMPOSITION OF SPENT SHALES FROM
HYDROGEN RETORTED SAMPLES (wt% dry basis)

Samples	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	BTU/lb
NB-1	0.75	3.05	0.21	0.02	0.60	3.4	107
NB-2a	0.35	1.98	0.26	0.06	0.22	0.10	170
NB-2b	0.17	0.90	0.16	0.05	0.30	<0.10	75
NB-3	0.47	1.58	0.20	0.06	0.19	<0.10	231
NB-4	1.26	1.95	0.25	0.03	0.19	6.0	116
NB-5	1.35	2.32	0.26	0.08	0.18	0.30	245
NB-6	0.53	3.18	0.17	0.04	0.52	11.30	94
NB-7	0.13	4.68	0.28	0.07	0.42	1.60	300
NB-8	0.39	2.85	0.29	0.10	0.14	6.20	403
NB-9	0.75	2.40	0.17	0.19	0.43	<0.10	341
NB-10	0.34	1.45	0.19	0.15	0.04	1.70	141
NB-11	0.01	3.42	0.12	0.19	1.79	<0.10	402
NB-12	0.29	1.98	0.12	0.18	0.83	<0.10	314
NB-13	0.18	1.55	0.19	0.06	0.52	<0.10	329
NB-14	0.60	2.05	0.06	0.03	0.86	1.40	238
NB-15	0.61	1.35	0.12	0.07	0.59	<0.10	195
NB-16	0.25	7.75	0.53	0.25	0.58	<0.10	616
ONT-1199	1.92	3.15	0.29	0.10	1.21	<0.10	547
ONT-1200	0.62	2.79	0.26	0.08	0.95	1.48	306

TABLE 7 CONTINUED

Sample	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	BTU/lb
ONT-1201	0.49	1.96	0.16	0.06	1.80	<0.10	449
ONT-55	2.59	1.93	0.81	0.15	1.34	1.50	380
ONT-C7A	3.35	2.17	0.80	0.22	0.63	14.90	150
NS-SP1	0.08	5.22	0.38	0.05	0.77	<0.10	832
NS-SP2	0.32	4.05	0.27	0.08	0.57	<0.10	607
NFLD-189-6	0.65	2.65	0.26	0.02	0.08	6.00	#
NFLD-189-10	0	3.75	0.23	0.03	0.03	7.20	32
BC-1	0.64	2.82	0.08	0.09	0.76	<0.10	489
QUE-1	1.25	0.75	0.17	0.09	0.47	<0.10	#
QUE-2	0.96	0.63	0.20	0.04	0.38	9.5	#
QUE-3	1.71	0.99	0.08	0.09	0.38	13.0	#
QUE-4	1.54	1.02	1.14	0.05	0.88	<0.10	#
QUE-5	1.35	1.22	0.16	0.06	1.11	<0.10	233
QUE-6	0.55	1.12	0.14	0.06	0.88	<0.10	123
QUE-7	0.06	0.90	0.20	0.05	0.75	<0.10	62
QUE-8	0.76	0.88	0.21	0.04	0.90	0.20	98
QUE-9	1.15	0.50	0.18	0.06	0.47	14.50	#
KT	0	3.15	0.12	0.02	0.64	<0.10	218

BTU/lb determined to be zero.

RESEARCH AND PRODUCTIVITY COUNCIL

TABLE 8

COMPOSITION OF SELECTED SHALE OILS FROM HYDROGEN RETORTING TESTS

Samples	Carbon wt %	Hydrogen wt %	Nitrogen wt %	Sulphur wt %	Oxygen wt %	BTU BTU/lb
NB-2a	85.76	11.12	0.70	0.55	1.87	18047
NB-5	85.33	11.06	0.66	0.55	2.40	18497
NB-9	86.62	11.02	0.53	0.50	1.33	18169
NB-11	87.63	10.93	0.73	0.40	0.31	18044
NB-16	85.14	11.21	0.56	0.50	2.59	17677
ONT-1199	87.50	9.70	0.45	1.05	1.30	15974
ONT-1200	87.49	10.34	0.63	1.60	<0.10	16962
ONT-1201	87.08	9.11	0.52	1.85	1.44	15896
NS-SP2	87.53	9.57	0.64	0.95	1.31	*12002
NFLD-189-6	87.53	10.76	0.56	1.80	<0.10	*15476
KT	87.41	10.09	0.60	1.20	0.70	17533

* Less than 0.1 gm of sample used in determination

TABLE 9

NITROGEN RETORT OF SELECTED OIL SHALES

Samples	Water wt %	Gas & Loss wt %	Oil wt %	Density g/ml	Oil gal/ton
NB-2a	4.1	5.1	6.2	------	14.4
NB-5	4.3	sample spill	7.9	0.8588	18.4
NB-9	2.4	5.9	7.4	------	17.2
NB-11	1.0	5.6	10.4	0.8602	24.2
NB-16	2.8	12.9	11.1	0.8537	25.8
ONT-1199	1.7	3.7	4.4	------	10.2
ONT-1200	0.9	5.0	3.2	------	7.4
ONT-1201	2.4	3.6	1.8	------	4.2
ONT-55	0.9	8.2	3.4	------	7.9
ONT-C7A	0.5	6.1	1.6	------	3.7
KT	4.1	4.1	3.6	------	8.4

------ insufficient sample to determine density

6.0 DISCUSSIONS AND CONCLUSIONS

6.0 DISCUSSION AND CONCLUSIONS

6.1 General

The Kentucky oil shale used for the optimization phase of the contract was evaluated at the Institute of Gas Technology, Chicago, Illinois. The results of the IGT evaluation can be found in Appendix 3. The organic carbon converted under hydroretorting conditions was 80.2 percent compared with 43.5 percent by Fischer assay. Similarly hydroretorting increased the oil yield to 15.0 gal/ton from 9.6 gal/ton for Fischer assay. The IGT results compared favourably with the results obtained with the optimized RPC facility; see Table 10. The RPC carbon conversion rate was 77.3 percent and the oil yield was 15.8 gal/ton.

TABLE 10

COMPARISION OF IGT AND RPC HYDROGEN RETORTING OF KENTUCKY OIL SHALE

	IGT	RPC
Organic Carbon Conversion (%)		
Hydrogen retort	80.2	77.3
Fischer assay	43.5	46.6
Nitrogen retort	----	43.1
Oil Yield (gal/ton)		
Hydrogen retort	15.0	15.8
Fischer assay	9.6	9.4
Nitrogen retort	----	8.4

The maximum oil yields for the Kentucky shale were recovered at 700°C and a hydrogen pressure of 500 psi.

An increase in hydrogen pressure from 100 psi to 500 psi resulted in a marginal increase in oil yield of only 10.4 percent as shown in Figure 6, however the total yields of gas and oil increased 26.4 percent. Similar trends have been obtained by IGT[1], on other oil shales, the magnitude of the effect depending on the sample. Average results[1] for the percent carbon conversion with increasing hydrogen pressure for Eastern U.S. New Albany shale and Western U.S. Colorado shale are given in Figure 8. The chemistry of the different kerogens, in particular hydrogen/carbon ratio as well as structural differences in the shales will play important roles in determining the response to pressure conditions.

The effect of increasing temperature on oil yield and total yield for the standard Kentucky shale is shown in Figure 7. The increase in the maximum hydroretorting temperature from 500°C to 700°C resulted in a 5.6 percent increase in oil yield and a 17.3 percent increase in the total yield of gas and oil. This may reflect a greater selectivity of organic carbon to gas at higher temperatures. It should be noted that carbonate decomposition can occur above 600°C and result in CO_2 production, however the Kentucky shale contained less than 0.03 percent mineral carbon and contributions to total gas generation due to its decomposition would have been minor.

The effect of increasing the heating rate was to decrease the yield of oil and gaseous products. This may have caused low oil yields for some retorting tests since heat-up rates were difficult to maintain constant. Heating rates faster than the optimum rate of 8°C per minute were recorded during parts of several runs. Estimated precision of heating rates were ±2°C/min on a per test time base, ±5°C/min on a one-half hour time base, and ±10°C/min on a five minute time base.

FIGURE 6: EFFECTS OF HYDROGEN PARTIAL PRESSURE ON OIL YIELD AND TOTAL YIELD

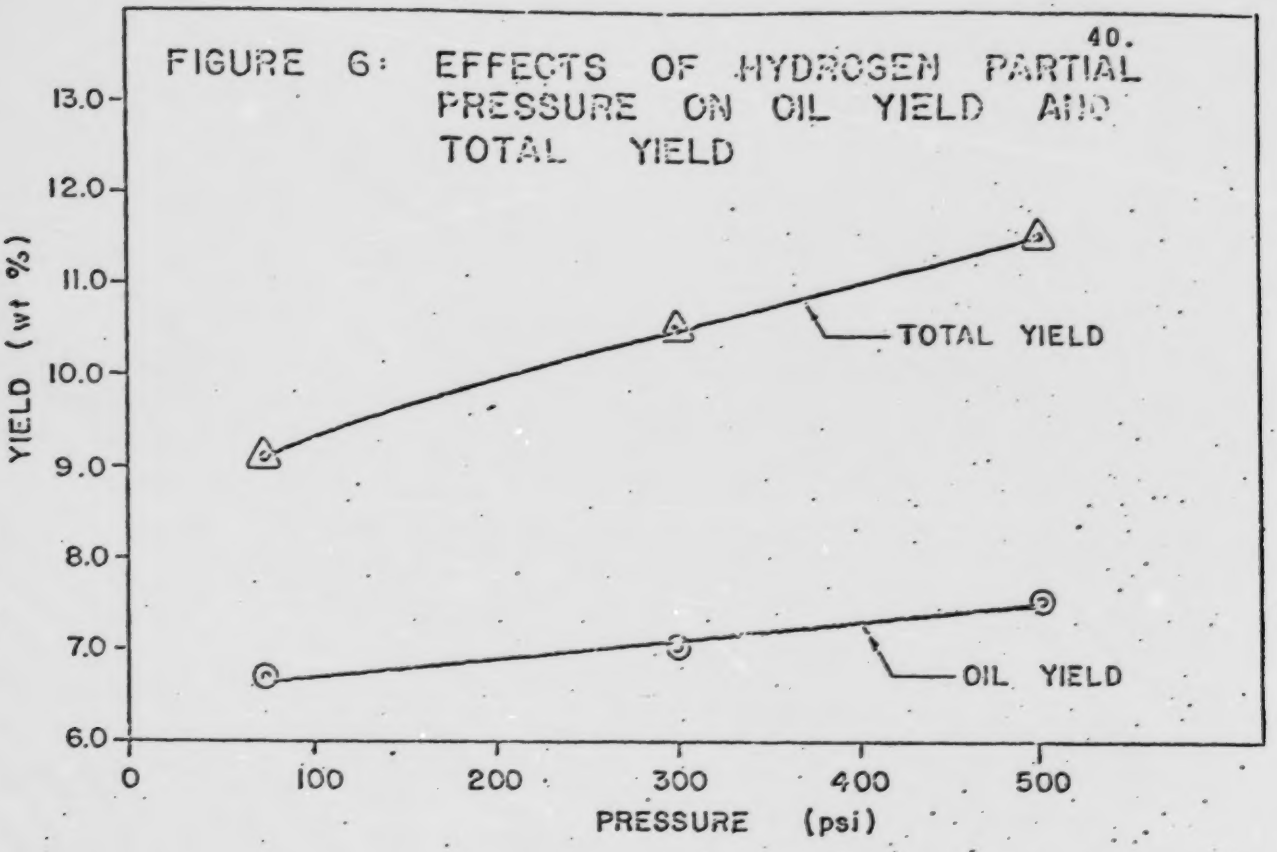


FIGURE 7: EFFECTS OF HYDRORETORTING TEMPERATURE ON OIL YIELD AND TOTAL YIELD

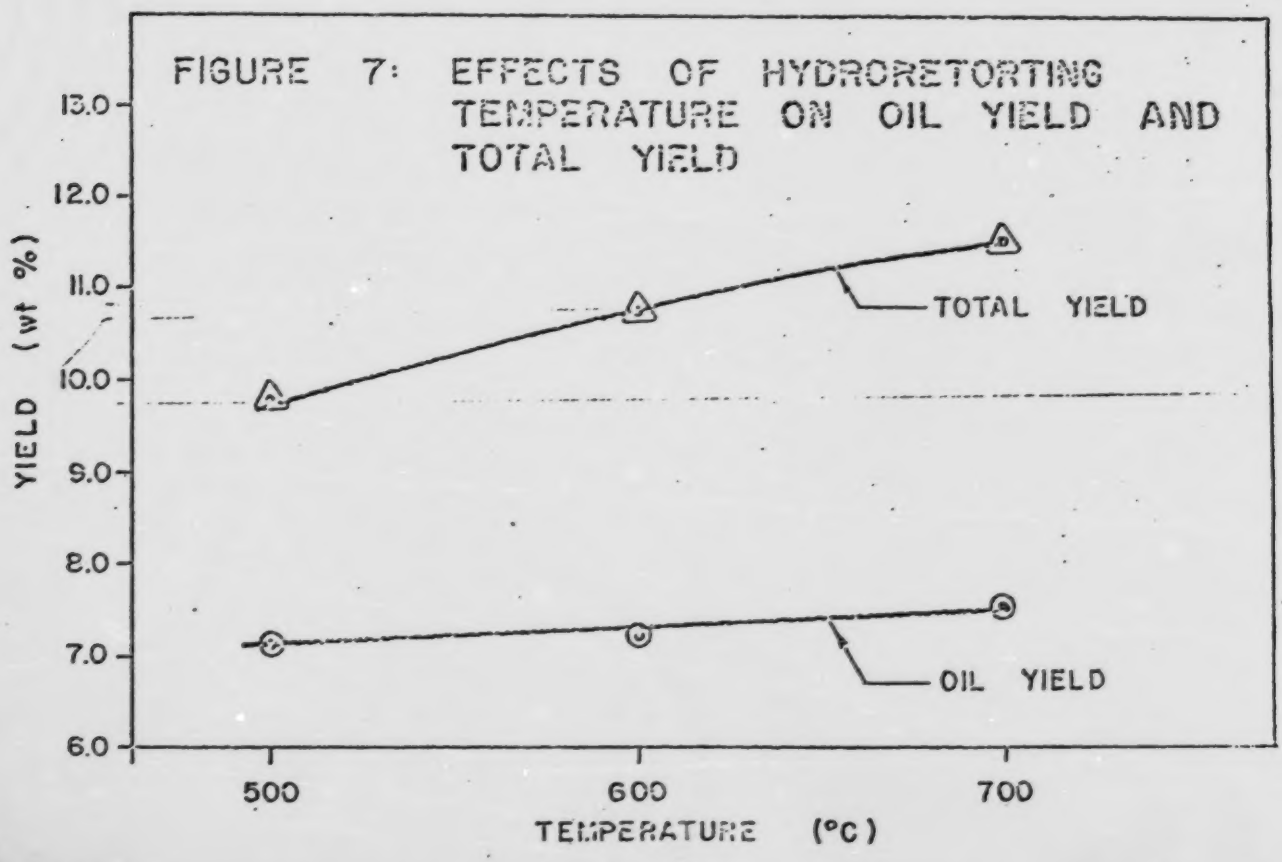
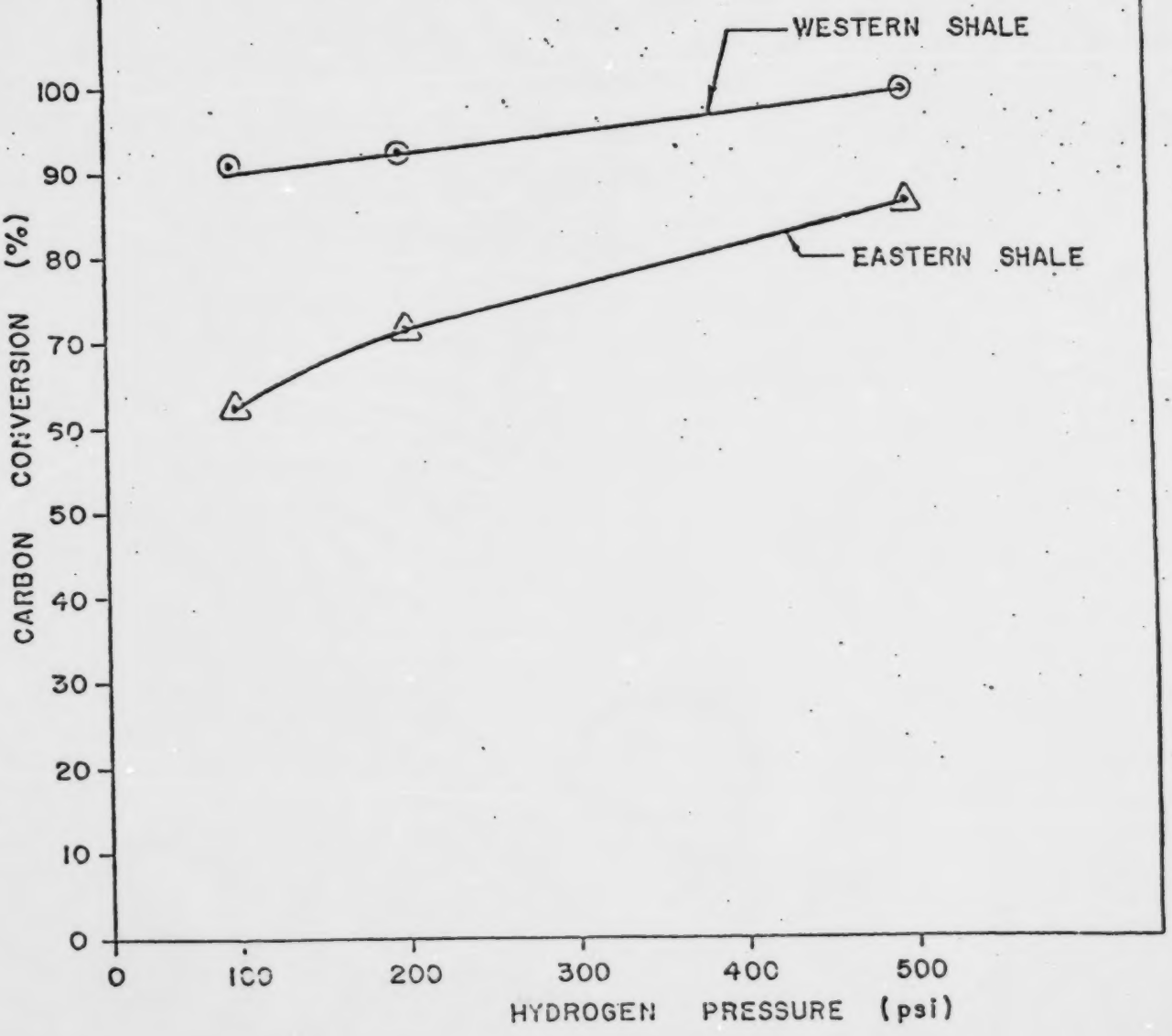


FIGURE 8: PARTIAL PRESSURE OF HYDROGEN VERSUS PERCENT CARBON CONVERSION FOR EASTERN AND WESTERN UNITED STATES OIL SHALE



Hydrogen retorting with the optimized facility increased the oil yields for all shale samples tested. Table 11 compares oil yields from selected hydroretorted samples with the samples retorted under identical conditions with 500 psi nitrogen. The nitrogen retorting gave oil yields of 3.7 to 25.2 gal/ton while hydrogen retorting gave yields of 7.1 to 46.2 gal/ton which corresponds to an average increase of 89.9 percent. Increases in organic conversion rates were also found as shown in Table 11; however, a simple relationship between conversion rates and oil yields could not be found.

Oil shale samples from the Albert area of New Brunswick gave the highest oil yields of all shales tested. Of the seventeen samples hydroretorted, five yields were greater than 30 gal/ton, and seven between 20 and 30 gal/ton. The average oil yield for all seventeen samples was 25.2 gal/ton which represented a 59.2 percent increase in oil yield over the Fischer assay method.

It should be noted that the oil yields in the Fischer assays were greater than in the nitrogen retorts and the gas yields were less. This may have been because the faster heating rate and higher pressure promote gas versus liquid product. The higher gas yields were also partially due to the breakdown of mineral carbon to CO_2 at 700°C. The average oil yields for the five New Brunswick samples retorted under nitrogen increased from 20.00 gal/ton to 38.4 gal/ton when retorted under hydrogen. This gave an average increase of 92.0 percent.

TABLE 11

CARBON CONVERSION RATES AND OIL YIELDS OF OIL SHALES RETORTED AT 500 PSI HYDROGEN AND 500 PSI NITROGEN

	Organic Carbon Conversion (%)		Oil Yields (gal/ton)		Ratio
	N_2	H_2	N_2	H_2	
NB-2a	72.1	90.1	14.4	32.9	2.28
NB-5	54.8	83.4	18.4	35.2	1.91
NB-9	60.2	87.3	17.2	32.2	1.87
NB-11	58.2	86.4	24.2	45.7	1.89
NB-16	63.9	80.8	25.2	46.2	1.79
ONT-1199	44.7	72.8	10.2	16.2	1.59
ONT-1200	47.6	73.4	7.4	11.9	1.61
ONT-1201	30.2	72.3	4.2	7.1	1.70
ONT-55	41.2	73.5	7.9	14.6	1.85
ONT-C7A	39.3	70.9	3.7	10.3	2.78
KT	43.1	77.3	8.4	15.8	1.88

7.0 ACKNOWLEDGEMENTS

7.0 ACKNOWLEDGEMENTS

The guidance and assistance of Mr. E. Furimsky of Energy, Mines, and Resources in the procuring of samples and in the layout of the experiemental program is recognized with appreciation.

Roy S. Boorman
Head: Mineral Development and Processing

Report Prepared By: J. Synnott/R. Salter

Report Approved by: R. Boorman

Test Program Completed By: J. Synnott/M. Maloney/A. Sharpe/W.Fowler/
R. Salter

8.0 REFERENCES

8.0 REFERENCES

1) WEIL, S. A., FELDKIRCHNER, H. L., PUNWANI, D. V., and JANKA, J. C., 1978. The IGT Hytort Process for Hydrogen Retorting of Devonian Oil Shales, Chattanooga Shale Conference, Nov. 14, 1978.

2) BROWN, G. P., and ABBOTT, D., 1981, Evaluation of Oil Shale from Eastern Canada by Retorting and by Concentration of a Kerogen-rich Fraction, CANMET Project Number 420 410, RPC Report Number AS/82/202.

3) STANFIELD, K. E. and FROST, I.C., Method of Assaying Oil Shale by a Modified Fischer Retort, U.S. Bureau of Mine Report of Investigations, R.I. 3977.

9.0 APPENDICES

APPENDIX 9.1

STATEMENT OF WORK

APPENDIX "A"

STATEMENT OF WORK

This work is a continuation of the first phase of the contract (construction of testing facilities and hydroretorting of oil shale from New Brunswick). The second phase should include the following tasks:

Task 1 Modification of the existing facilities.

Following changes shall be made according to the Scientific Authority's instructions

- shortening of the tube connecting the retort and pressure reducing valve.
- shortening of the tube connecting the pressure reducing valve, and liquid products receiver.
- controlling the temperature, in the vicinity of the valve, at about 200° C.

Task 2 Optimization of hydroretorting conditions.

The following steps should be further investigated:

- hydroretorting at 500°C, 550°C, 620°C and 700°C should be conducted.
- effect of particle size should be investigated (three different sizes)
- hydroretorting under 100 and 300 psi of hydrogen in addition to 500 psi will performed.
- retorting of different amounts of sample (e.g. 50g and 100g) will be compared.
- retorting under nitrogen will be used as a base to compare beneficial effects of hydrogen.

For this phase of the work, an oil shale sample with defined characteristics and a significant response to hydroretorting will be used. Thus, an oil shale sample from U.S. (e.g. Kentucky shale) will be acquired. Hydroretorting will be evaluated at IGT. This sample will be used as the standard to test and calibrate the facilities.

Characterization of the materials should include the following analysis:

raw shale - mineral carbon content, ultimate analysis, fingerprinting by pyrolysis - gas chromatography, determination of soluble matter content, heating value and mineral constituents.

spent shale - ultimate analysis, heating value and mineral carbon content.

liquid products - C, H, N, S, and O contents, spec. gravity.

gases - component analysis of one sample taken at a middle point of retorting.

Task 3 Evaluation of Oil Shales from Different Provinces

At this stage the samples from the Provinces Of Ontario, Quebec, Nova Scotia and Newfoundland will be evaluated. The screening will be performed according to the conditions established in the Task 2. Each hydroretorting test will be complemented by the Fischer assay. Total of 25 samples will be evaluated. The selection of the samples will be made in consultations with the Scientific Authority and should include the following formations:

APPENDIX "A" - page 2

Ontario	- North Shore Lake Georgian Bay Billings (Ottawa area) Cobourg Lake Erie (Marcelus formation) Kettle Point Long Rapids
Quebec	- Trois Rivier Montreal (Orleans Island) Gaspe Peninsula (York River)
Nova Scotia	- Stellarite (Stellarton) Big Marsh (Antigonish) Pictou (McLellan Brook)
Newfoundland	- Deer Lake Humber River

After this phase of the Task 3 is completed, a detailed evaluation of the experimental data will be made. The samples giving high yields of liquids during hydroretorting, compared to that from the Fischer assay, will be identified. These samples will, then be retorted at the same temperature but under nitrogen.

Task 4 Evaluation of Oil Shales from the Province of New Brunswick

It is anticipated that additional samples from the Province will be characterized. The evaluation should be performed in connection with oil shale exploration and inventarization carried on in New Brunswick. This work will be performed on a continuous basis in the course of the contract work. About 15 samples will be evaluated. The attention will be paid to samples from the most pospective areas.

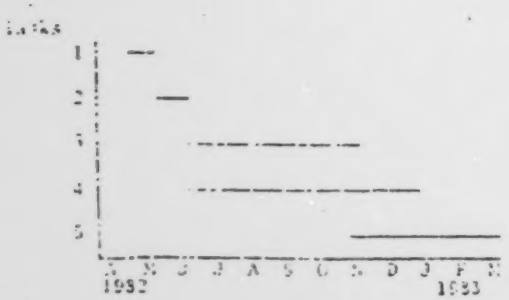
The main purpose of this task is to contribute to a better understanding of oil shale as a potential source of liquid fuels in the Province of New Brunswick.

Task 5 Preparation of Final Report

A tabulation and interpretation of the experimental data will proceed the preparation of the first draft of the report. Essential parts of the report should be:

1. Detailed description of experimental procedure
2. Properties of feedstocks and all products (yields including) from samples identified in Task 3.
3. Properties of feedstocks and all products (yields including) from samples identified in Task 4.
4. Recommendations which follow from the study.

TIME SCHEDULE



APPENDIX 9.2

SAMPLE DETAILS

NEW BRUNSWICK SAMPLES

Sample	Location	Description
NB-1	outcrop #V23-15, MAP-NB#1	Dark grey, brown weathering, subfissile, dolomitic, kerogenous shale. Rock is laminated but not papery. Rock adds to flame but will not burn.
NB-2a	outcrop #V23-18, (south end) MAP-NB#1	Dark grey, flexible, papery, slightly dolomitic, kerogenous shale. Rock burns unassisted after ignition.
NB-2b	outcrop #V23-18, (centre) MAP-NB#1	Dark grey, crumbly subconchardal fracturing, slightly dolomitic mudstone. Rock adds slightly to flame but will not burn.
NB-3	outcrop #V23-37, MAP-NB#1	Dark grey, brown-weathering, flexible papery, dolomitic, kerogenous shale. Rock burns unassisted after ignition.
NB-4	outcrop #V23-40, MAP-NB#1	Dark grey, fissile, papery, calcareous and dolomitic shale. Rock will just burn unassisted.
NB-5	outcrop #V23-41, MAP-NB#1	Dark grey, brown weathering, papery, dolomitic shale. Rock will burn unassisted after ignition with relative ease.

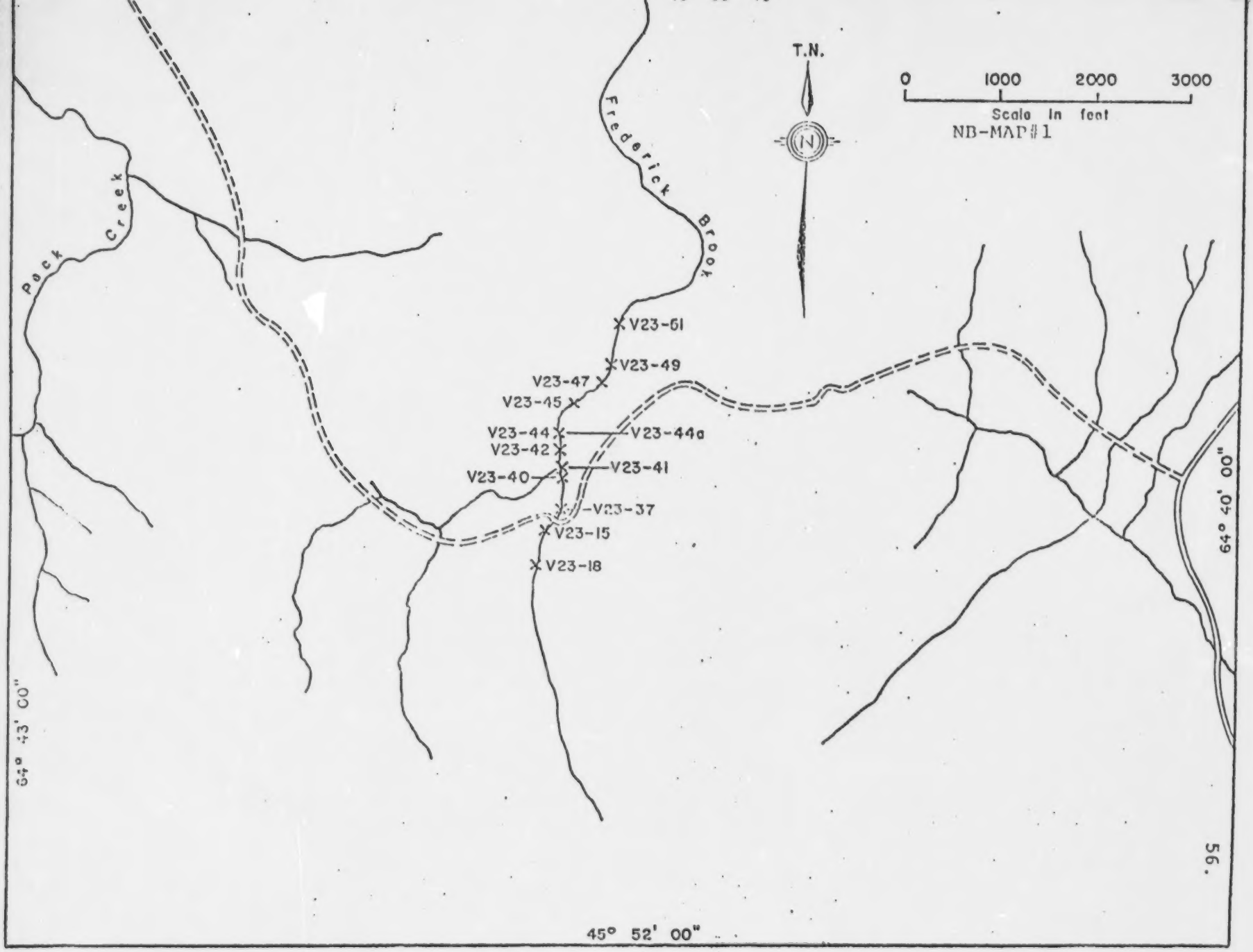
RESEARCH AND PRODUCTIVITY COUNCIL

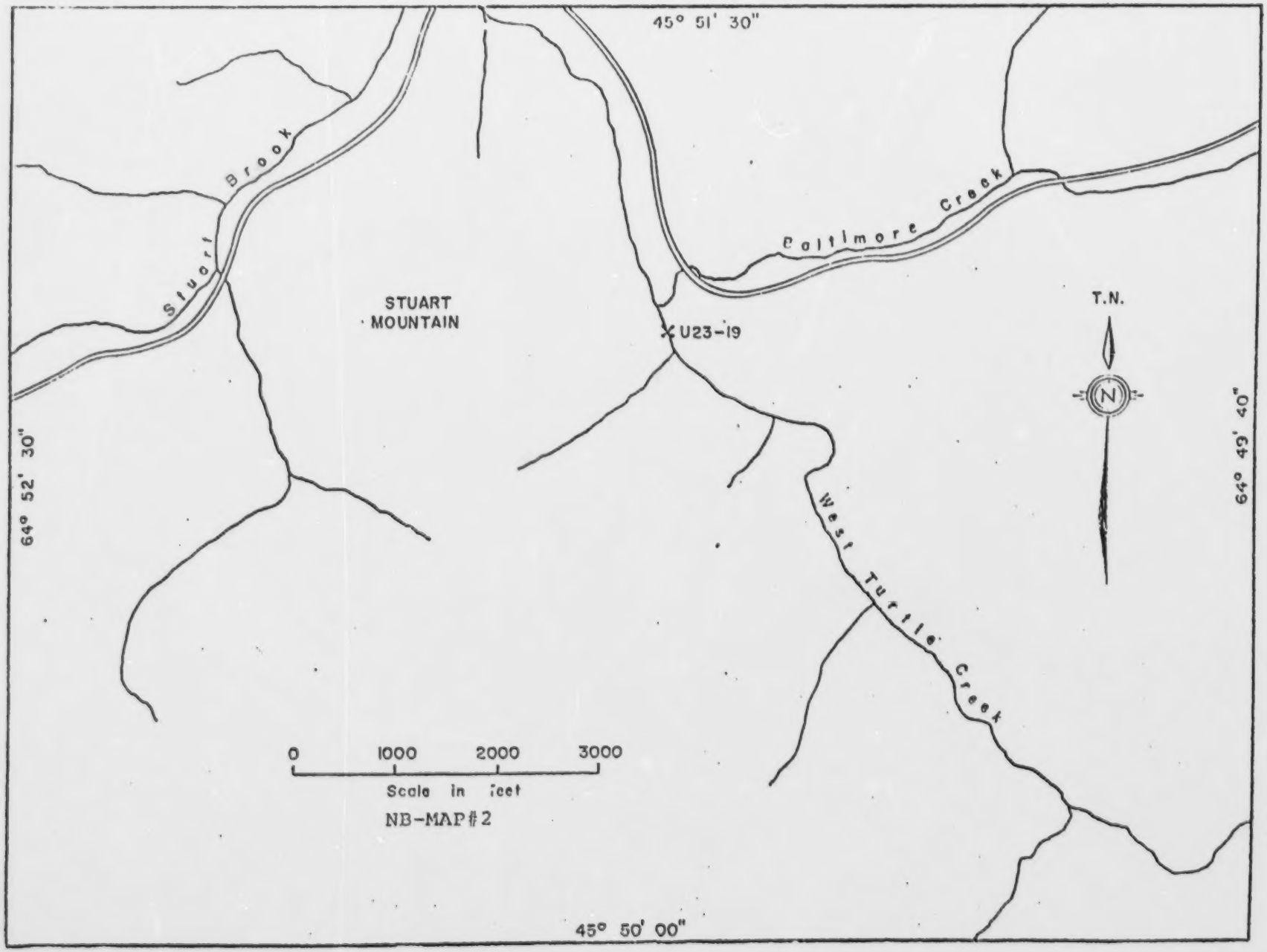
NEW BRUNSWICK SAMPLES

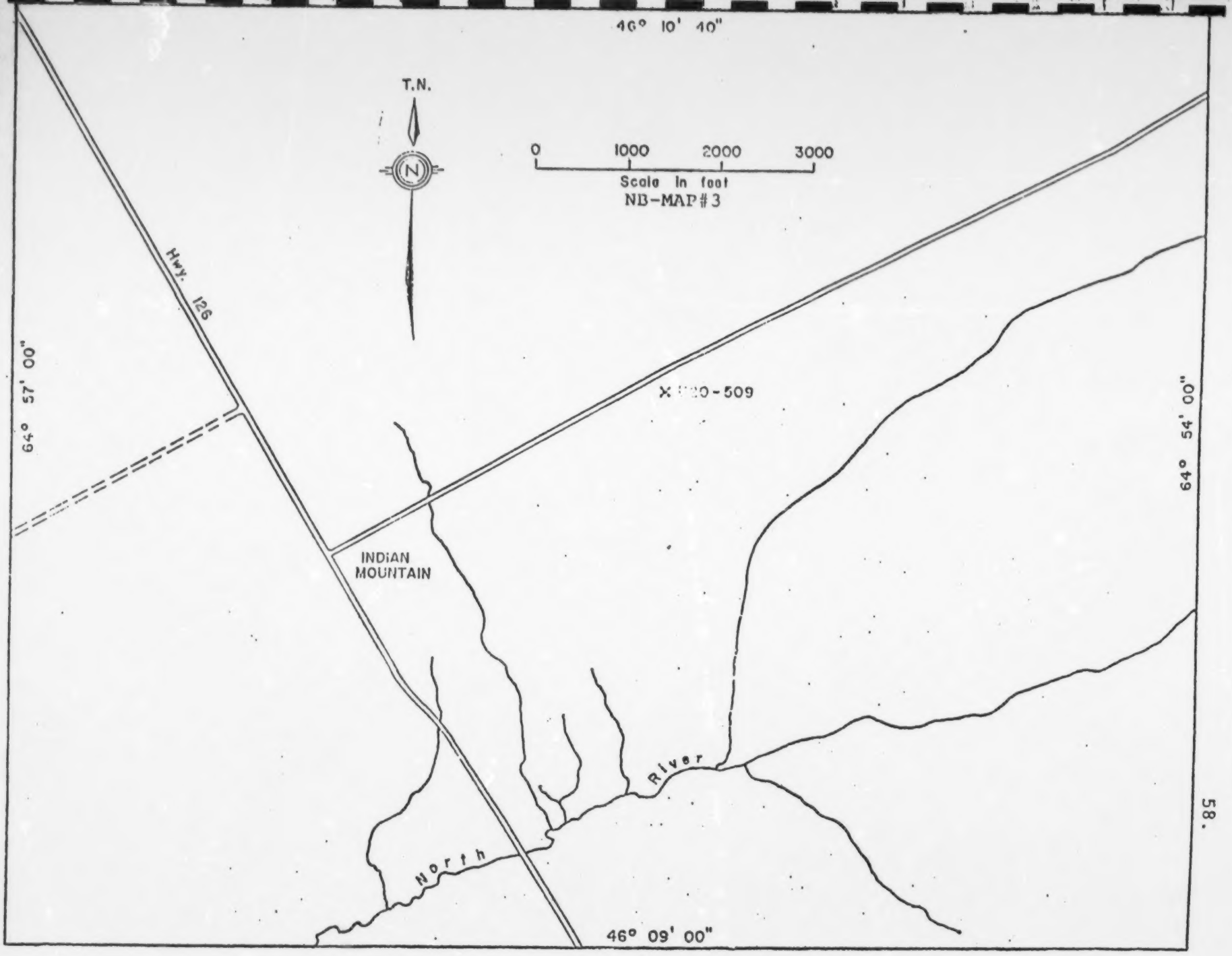
Sample	Location	Description
NB-6	outcrop #V23-42, MAP-NB#1	Dark grey brown weathering, papery, dolomitic shale. Rock will burn unassisted after ignition with relative ease.
NB-7	outcrop #V23-44, MAP-NB#1	Dark grey brown weathering, blocky, parallel-laminated, dolomitic marlstone. Rock contains sedimentary mesoscopic folds. Rock will just burn unassisted after ignition.
NB-8	outcrop #V23-44a, MAP-NB#1	Dark grey, brown-weathering, blocky, parallel-laminated, dolomitic marlstone. Rock will burn unassisted after ignition.
NB-9	outcrop #V23-45, MAP-NB#1	Dark grey, brown-weathering, blocky, parallel-laminated, slightly dolomitic marlstone. Rock will burn unassisted with ease.
NB-10	outcrop #V23-47, MAP-NB#1	Dark grey, brown-weathering, blocky, parallel-laminated, slightly dolomitic marlstone. Rock will burn unassisted with ease.
NB-11	outcrop #V23-49, MAP-NB#1	Dark grey, brown-weathering, massive, moderately dolomitic siltstone. Rock will just burn unassisted after ignition.

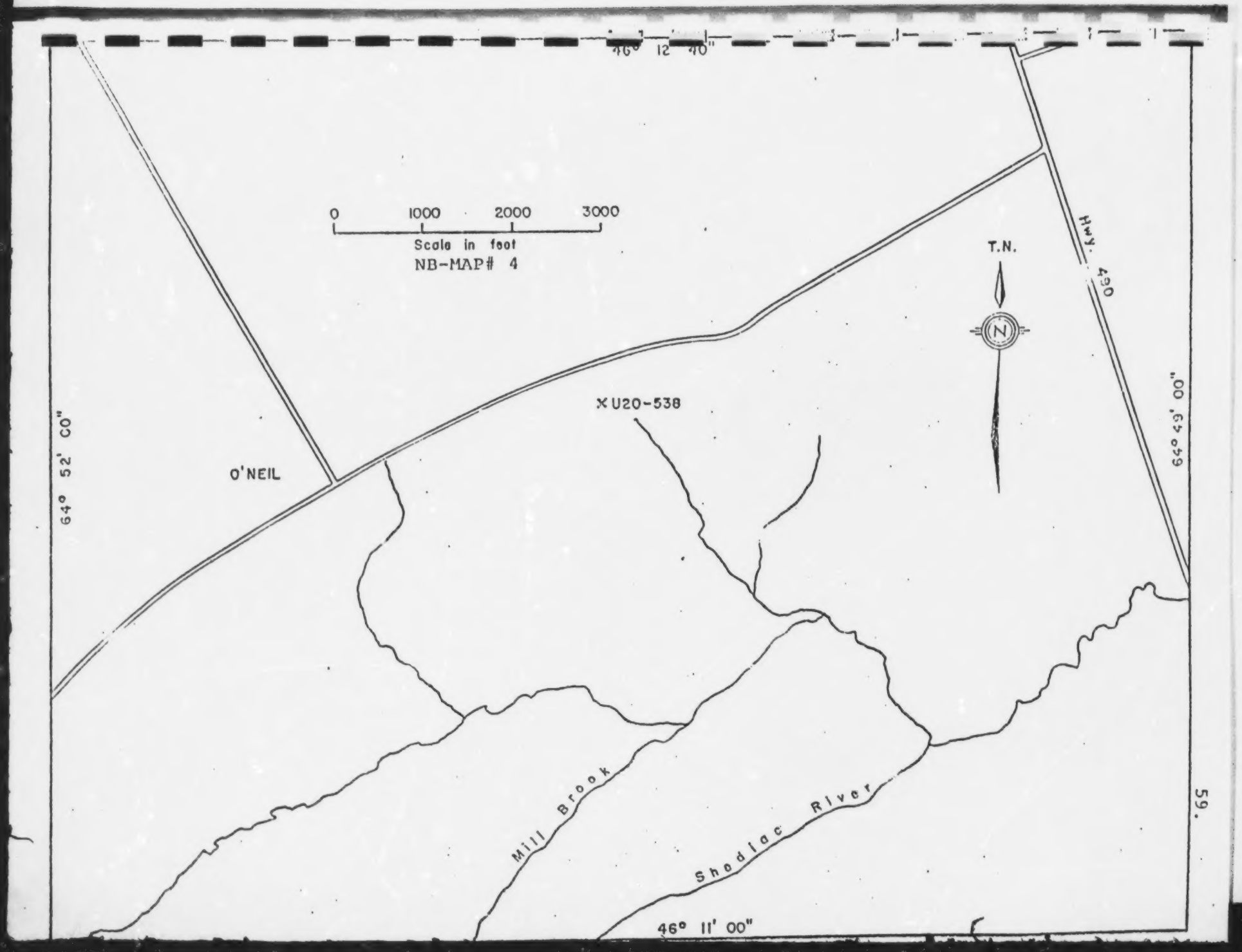
NEW BRUNSWICK SAMPLES

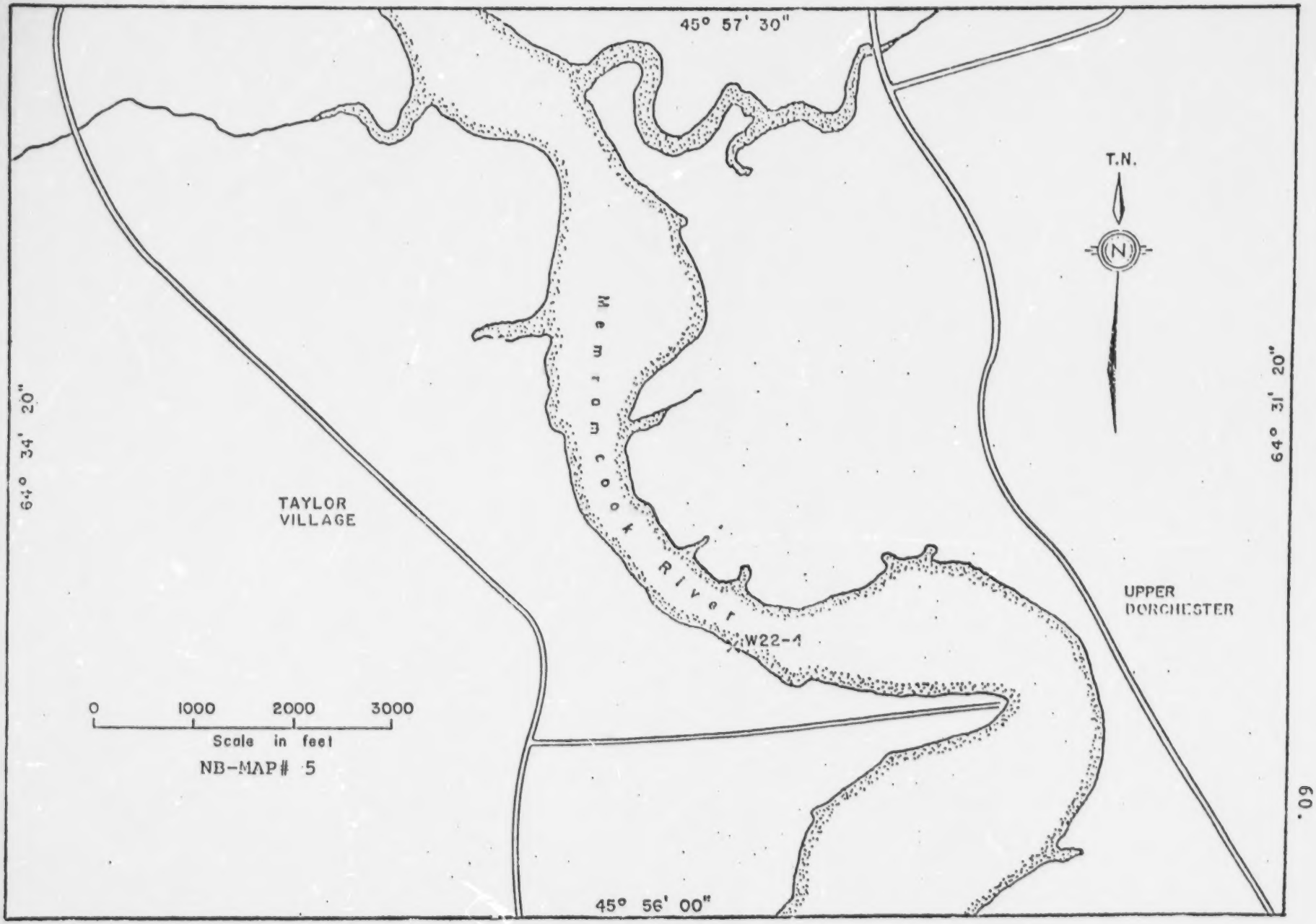
Sample	Location	Description
NB-12	outcrop #V23-51 MAP-NB#1	Dark grey, brown-weathering, blocky, parallel-laminated, dolomitic marlstone. Rock will burn with relative ease after ignition.
NB-13	outcrop #U23-19 MAP-NB#2	Dark grey, brown weathering, subfissile, dolomitic siltstone. Rock will just burn after ignition.
NB-14	outcrop #U20-509 MAP-NB#3	Dark grey, brown-weathering, subfissle, highly dolomitic siltstone. Rock will just burn unassisted after ignition.
NB-15	outcrop #U20-538 MAP-NB#4	Dark grey, siltstone with parallel laminations of brown-weathering, light grey, very fine-grained sandstone. Rocks very slightly dolomitic.
NB-16	outcrop #W22-4 MAP-NB#5	Brown, compact, competant, dolomitic blocky marlstone. Rock displays irregular wispy hair-line curly layers of low reflectance dark grey kerogen. Rock burns with relative ease.


T.N.
0 1000 2000 3000
Scale in feet
NB-MAP#1
Pock Creek
Frederick Brook
V23-61
V23-49
V23-47
V23-45
V23-44
V23-44a
V23-42
V23-41
V23-40
V23-37
V23-15
V23-18
64° 43' 00"
64° 40' 00"
45° 52' 00"
56


45° 51' 30"
Stuart Brook
Baltimore Creek
STUART
MOUNTAIN
U23-19
T.N.
N
64° 52' 30"
64° 49' 40"
West Turtle Creek
0
1000
2000
3000
Scale in feet
NB-MAP#2
45° 50' 00"


46° 10' 40"
T.N.
N
0
1000
2000
3000
Scale in feet
NB-MAP#3
Hwy. 126
64° 57' 00"
64° 54' 00"
INDIAN
MOUNTAIN
River
North
46° 09' 00"


46° 12' 40"
0 1000 2000 3000
Scale in feet
NB-MAP# 4
T.N.
N
Hwy. 490
64° 49' 00"
64° 52' 00"
O'NEIL
X U20-538
Mill Brook
Shediac River
46° 11' 00"


45° 57' 30"
T.N.
N
64° 34' 20"
64° 31' 20"
TAYLOR
VILLAGE
Memramcook River
W22-1
UPPER
DORCHESTER
45° 56' 00"
0 1000 2000 3000
Scale in feet
NB-MAP# 5

ONTARIO SAMPLES

Sample	Location	Description
ONT-1199		
ONT-1200		
ONT-1201		
ONT-55		
ONT-C7A		

INFORMATION NOT SUPPLIED BY SCIENTIFIC AUTHORITY

NOVA SCOTIA AND NEWFOUNDLAND SAMPLES

Sample	Location	Description
NS-SP1	Pictou County, Nova Scotia - shale on the pavement and between the two torbanite beds in Shaw Pit, MAP-NS#1	- thinly laminated, very friable, dark brown streak when scratched, rustic appearance on weathered surface
NS-SP2	Pictou County, Nova Scotia Shaw Pit, shale underlying till cover, MAP-NS#1	- blocky in nature, splits easily along bedding planes, greasy feel, dark brown streak, dark on weathered surface, slightly friable, contains plant fossils
NFLD-189-6	Deer Lake, Humber River, Newfoundland, upper part of Rocky Brook formation MAP-NFLD#1	
NFLD-189-10	Deer Lake, Humber River, Newfoundland, upper part of Rocky Brook formation MAP-NFLD#1	

OIL SHALE SAMPLES FROM PICTOU COUNTY

The oil shales in Pictou County occur in the late Carboniferous Stellarton Group which also contains the productive coal measures of the Pictou coalfield.

The oil shales are exposed along the banks of McLellans Brook and in the Shaw clay pit.

The sample locations were chosen in areas that were considered worthy of further attention by Swinnerton in his report on the oil shales.[1]

The samples from the Shaw pit (SP-1, 2, 3) should correspond closely to Swinnerton's location AB while the McLellans Brook sample was taken from location D. It may be noted here that although the sample locations are close they need not be the same outcrops as mentioned in the report.

The following is a brief description of the samples (see diagram for Shaw Pit sample locations).

Sample SP-1 — The sample represents the oil shale on the pavement and between the two torbanite beds in the Shaw Pit. The shale is thinly laminated and very friable and gives a dark brown streak when scratched. It has a rusty appearance on the weathered surface. Approximately 8 - 10 kg sample taken.

Sample SP-2 — The sample represents the oil shale underlying till cover. It is blocky in nature but splits easily along bedding planes. It has a greasy feel and exhibits a dark brown streak. It is dark on the weathered surface and only slightly friable. The shale contains plant fossils. Approximately 8 - 10 kg sample taken.

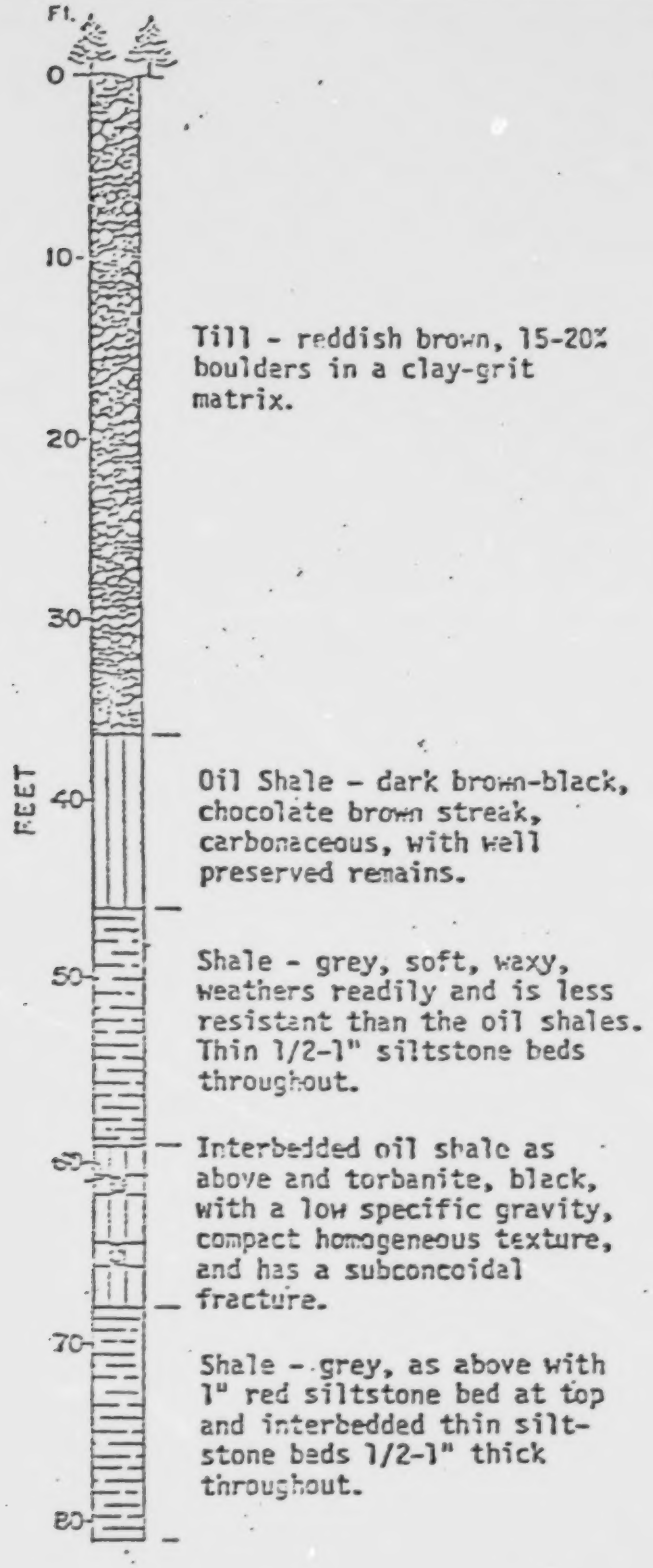
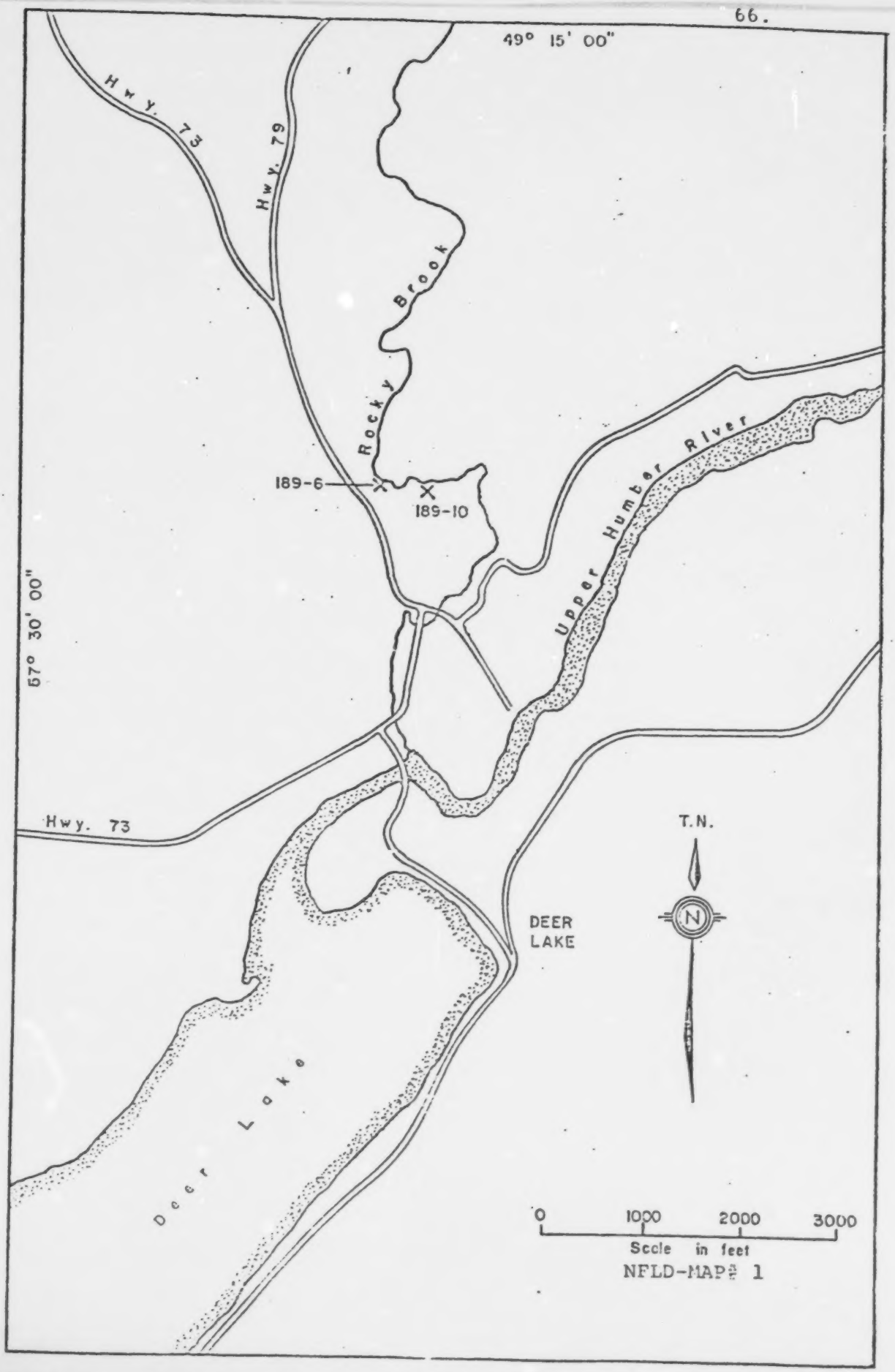

Ft.
0
10
20
30
40
50
60
70
80
FEET
Till - reddish brown, 15-20% boulders in a clay-grit matrix.
Oil Shale - dark brown-black, chocolate brown streak, carbonaceous, with well preserved remains.
Shale - grey, soft, waxy, weathers readily and is less resistant than the oil shales. Thin 1/2-1" siltstone beds throughout.
Interbedded oil shale as above and torbanite, black, with a low specific gravity, compact homogeneous texture, and has a subconcoidal fracture.
Shale - grey, as above with 1" red siltstone bed at top and interbedded thin siltstone beds 1/2-1" thick throughout.

Figure 21. Section through 'Shaws Pit' in Pictou coalfield - field stop 7 (compiled by W. Potter in 1978).

NS-MAP-1
Trenton Airfield
Fraser Mountain
Fraser Mountain
Linacy
Riverton
Sutherland Bog
Terrace Heights
The Meadows
Pictou Rd
Trans-Can
STELLARTON
Blue Acres
Pleasant Park
Plymouth
Mountville
Satellite Slopes
McGregor Mountain
Riverton
Coalburn
Gun Club
SAMPLE
McLellans Brook
McLELLAN
Churchville
MAP 11E/10 1:50000


49° 15' 00"
Hwy. 73
Hwy. 79
Rocky Brook
189-6
189-10
Upper Humber River
67° 30' 00"
Hwy. 73
T.N.
N
DEER LAKE
Deer Lake
0 1000 2000 3000
Scale in feet

NFLD-MAP# 1

ECONOMIC GEOLOGY
NEWFOUNDLAND SAMPLES

In the investigation of the economic possibilities of the shale areas, the following method was employed. Channel samples were cut of each bituminous bed. Shale samples were roughly tested in the field by fire test. Each sample from beds three feet and over in thickness, that gave off a smell of oil on heating and ignited either at low or high heat, was kept. These samples were then grouped under the following divisions.

1. Beds over three feet in thickness that ignited and burned readily at low heat.

2. Beds over three feet in thickness that ignited and burned at medium heat.

3. Beds over three feet in thickness that ignited and burned at high heat.

Group #1 - 20 beds, (8 Deer Lake, 8 Humber, 4 Grand Lake), varying from 3 to 5.2' in thickness.

Group #2 - 4 beds, (all on Rocky Brook), varying in thickness between 3 to 5.6'.

Group #3 - 6 beds, (all on Rocky Brook), varying in thickness from 3 to 6'.

The total number of beds selected for further testing was 30. Tests were made on eighteen of these, for volatile matter and moisture combined.

Tests on five for volatile matter, moisture, fixed carbon and ash.

Tests on two for actual Oil Yield.

A ratio between Volatile matter and oil yield was obtained on Deer Lake-Humber River shales and also on Grand Lake shales. The ratio for Deer Lake-Humber River was .63 Imperial gallons per ton for each percent of volatile matter. The ratio for Grand Lake shales was one Imperial gallon per ton for each percent volatile.

The results obtained were as follows: Actual Oil Yield from two samples.

7.5 Imperial gallons per ton. (Deer Lake)
10.5 Imperial gallons per ton. (Grand Lake)

Average percentage of volatile matter - Deer Lake Shales.

(14 samples) 9.27%

Actual Average Oil Yield (calculated) 5.84 gallons.

Average percentage volatile matter - Humber River Shales
(2 samples) 9.83%

Actual average Oil Yield (calculated) 6.19 gallons.

Average percentage volatile matter - Grand Lake Shales
(3 samples) 10.84%

Average Oil Yield (calculated) 10.8 gallons

Note: A shale to be commercial may be defined as a bed with a thickness greater than three feet, with an actual Oil Yield of more than 16 Imperial gallons per ton, and a yield of Ammonia Sulphate of 50 lbs. per ton.

It is certain that, as far as the investigation of these areas has gone, that no beds, where sampled, gave sufficient Oil Yield to be commercial. Conditions of sedimentation, however, varied greatly over the area and it is possible that other sections of the beds sampled would give a commercial yield.

The throwing out, as far as testing purposes goes, of all shale beds under three feet in thickness, is justified, as a thin bed would have to be very rich to pay. None of the thin beds indicated richness.

The presence of shale beds of the curly variety in the Grand Lake area, taken together with the great thickness of the shale series that is concealed, makes it impossible, without further investigation, to state definitely whether or not this area has commercial possibilities.

The exposures of the Deer Lake-Humber River series are practically continuous and the most careful work in the field has failed to uncover any high yield bed.

The Grand Lake area is, in the opinion of the writer, more likely to contain beds of commercial value than the Deer Lake-Humber River area.

Conclusions

Thin beds of petroliferous shale of low yield occur scattered through the uppermost part of the section. It is thought from the observations of the outcrops around Deer

Lake and in the Humber valley between the falls that no beds of oil shale of either sufficient thickness of sufficient richness for exploitation occur in the section.

BRITISH COLUMBIA AND KENTUCKY SAMPLES

Sample	Location	Description
BC-1	Queen Charlotte Island Oil Shale, Jurassic Kunga Formation (upper banded member) Ghost Creek Area	Organic carbon contant = 6.4% Pyrolysis recoveries = 24 U.S. gal/ton from Rock-eval techniques
KT	Fleming County, Kentucky 38°13'N Lat., 83°36'W Long. 25 ft. below the top of the Cleveland Member of the Upper Devonian Oil Shale - few thousand feet west of site D-11.	Reference - Geochemistry of the New Albany, Ohio and Sunbury Shales in East Central Kentucky - Stratigraphy and Resource Assessment of the Oil Shales of East Central Kentucky

Geochemistry of the New Albany, Ohio and Sunbury Shales in East Central Kentucky

by

Alan E. Bland
Thomas L. Robl
D.W. Koppenaal
Institute for Mining & Minerals Research
University of Kentucky

Introduction

Resource assessment work in Lewis and Fleming Counties, Kentucky has indicated that Kentucky oil shales are potential synthetic fuel feedstocks. A summary of this previous work is presented in another paper at this symposium (1). The Institute for Mining and Minerals Research (IMMR) of the University of Kentucky is continuing this work throughout the oil shale outcrop with support from the U. S. Department of Energy and the Kentucky Department of Energy. This paper presents our evaluation to date of the oil shales in the east-central portion of the central Kentucky outcrop belt. It includes the analysis of shales from Rowan, Bath, Montgomery, Powell, and Estill Counties, Kentucky, and a comparison with data obtained earlier on the Lewis-Fleming County shales. Stratigraphic and geochemical data were obtained to provide: 1) basic information to assess the nature of the oil shale as a synthetic fuel feedstock; 2) preliminary information on the potential for by-product recovery; and 3) preliminary information on the reclamation and environmental characteristics of the resource.

Project Sampling and Analysis

Eleven NX cores were drilled near the outcrop in a northeast-southwest trending line in Rowan, Bath, Montgomery, Powell, and Estill Counties (D-series of Figure 1). The coring was continuous with the Lewis-Fleming County work to the north (2), and was concentrated in regions which have potential for surface mining. Sample analysis was comparable to that used in the Lewis-Fleming County work.

The cores were described and measured in the field and returned to the Kentucky Center for Energy Research Laboratory. Each core was sawed in half and samples collected on a 2- to 6-foot interval basis. A total of 692 samples were generated. Each sample was jaw crushed to approximately -1/4 inch and roller-milled to approximately -10 mesh. Two 250-gram fractions were riffled out of each sample. One fraction was retained for Fischer Assay, and the second was reduced by ring and puck grinder to -350 mesh. Moisture, ash, carbon, hydrogen, nitrogen, and sulfur analyses were performed on the finely ground fraction. Ash determinations were performed at 500°C to prevent the volatilization of trace elements. Major element oxide and trace element determinations were performed on the 500°C ash fraction by X-ray fluorescence using international rock and mineral standards for calibration.

Oil Shale Stratigraphy

The stratigraphy and lithologies of the oil shale units and associated strata are discussed in detail in a previous paper at this symposium (1) and only a summary is presented here. The principal units of interest include (top to bottom) the Sunbury Shale (an oil shale), the Bedford Shale (a gray clay shale), and the Ohio Shale. The Ohio is divided into the Cleveland Member, the Three Lick Bed, and the Huron Member. These units are primarily oil shales; however, the Three Lick Bed and the lower Huron are significantly thick with barren, bioturbated, green-gray shales.

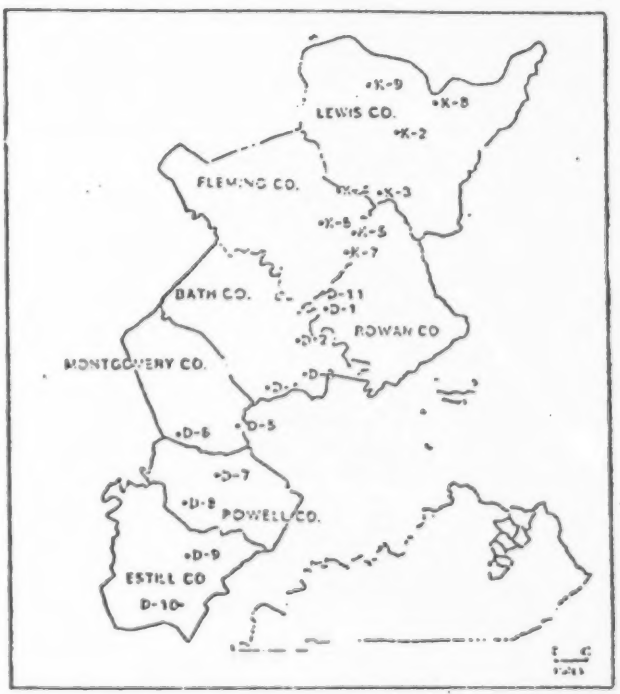


Figure 1. Distribution of Cores in the Study Area (D Series of Rowan, Bath, Montgomery, Powell, and Estill Counties) With Distribution of Cores From Previous Work (K-Series of Lewis and Fleming Counties).

Stratigraphy and Resource Assessment of the Oil Shales of East Central Kentucky

by

Don Pollock
Lance Barron
Institute for Mining & Minerals Research
University of Kentucky
John Beard
Kentucky Geological Survey

Abstract.

Heightened interest in the organic rich shales of Mississippian and Devonian age as a source of oil has resulted in intensive leasing along the shale outcrop belt in Kentucky. Eleven cores of the black shales from the counties of Rowan, Bath, Montgomery, Powell, and Estill were examined and analyzed in an effort to relate details of stratigraphy to the oil rich horizons and to indicate areas of potential resources. This report will not treat Estill County regarding the resource assessment.

Formations of interest are the Sunbury Shale (Early Mississippian Age) and the Ohio Shale (Late Devonian age). The name, Ohio Shale, is used throughout this report, but it was mapped as the New Albany Shale in the southern part of the study area by the U. S. G. S. The generalized stratigraphy (Early Mississippian through Middle Devonian age) is, in descending order: Borden Formation, Sunbury Shale, Bedford Shale, and Ohio Shale. Useful key markers in the sequence are the Three Lick Bed and Foerstia zone; which are both in the Ohio Shale. The Three Lick Bed divides the Ohio Shale into the Cleveland Member, above, and the Huron Member, below. The Ohio Shale is underlain by the Middle Devonian Boyle Dolomite or the Silurian Bisher Dolomite, or the Crab Orchard Formation, also Silurian in age.

The organic content is highest in the Sunbury Shale and in the Cleveland Member of the Ohio Shale. In the cores, the total thickness of the Sunbury Shale range from 17 to 4 feet (5.2 to 1.2 m). The thickness of the Bedford Shale, ranges from 18.0 to .2 feet (5.5 to .1 m). The Cleveland Member of the Ohio Shale ranges from 49.0 to 33.0 feet (14.9 to 10.1 m.).

Assuming a stripping ratio of 2.5:1, more than 4.5×10^5 acre-ft of shale having a carbon value of greater than 8% is minable by means of existing methods. A conservative estimate of the amount of the potential strippable shale-oil resources in the four county area is 3.80×10^9 bbls.

Introduction

Scientists have been studying the Devonian-Mississippian black shales of Kentucky from the time of the first Geological Survey in the Middle of the 19th Century (1). Since then they have been predicting that oil from this oil shale would become a source of illuminating oil (2), lubricant (3), natural gas (4), and refinery feedstocks (5, 6, 7, 8) in the near future. In the past, the principal focus of interest, has been on the western shales of Utah, Wyoming and Colorado. Within the last few years significant interest has developed in the Devonian-Mississippian oil shales of Kentucky and neighboring states. Social, geographical, and institutional barriers to development in the West have, in part, helped to create this interest.

QUEBEC SAMPLES

Sample	Location	Description
QUE-1	Neuville, road cut on Route No. 138, 2 km west of the Neuville Wharf	Lower Utica Shale
QUE-2	Cap Santé, road cut on Route No. 138, 2.7 km west of Cap Santé	Lower Utica Shale
QUE-3	Ste-Anne-de-la-Pérade road cut on Route No 138, 3.5 km east of Ste-Anne-de-la-Pérade	Middle part of Lower Utica Shale
QUE-4	St-Louis-de-France, riverbank cut on the left bank of St-Maurice River; 4 km SW of St-Louis de France (near intersection of Des Chenaux and Ste-Marguerite-West Roads)	Upper Utica Shale
QUE-5	L'Ephiphanie, End of Avenue Lussignon Riverbank Cut, right bank of L'Achignon River	Upper Utica Shale

QUEBEC SAMPLES

Sample	Location	Description
QUE-6	Ville Lasalle, Riverbank Cut on the north bank of the St. Lawrence River, intersection of Blvd. Lasalle and 6th Avenue	Upper Utica Shale
QUE-7	Delson, Riverbank Cut, on the right bank of Rivière à la Tortue which passes near the eastern limit of Delson	Upper Utica Shale
QUE-8	Pointe-au-Platon, Rivervank Cut, 1.6 km west of Pointe-au-Platon	Lotbinière Formation Shale
QUE-9	Chûtes Montmorency, about 18 km NE of Quebec City at the mouth of the Montmorency River, riverbank cut on the NE side of river	Lower Utica Shale

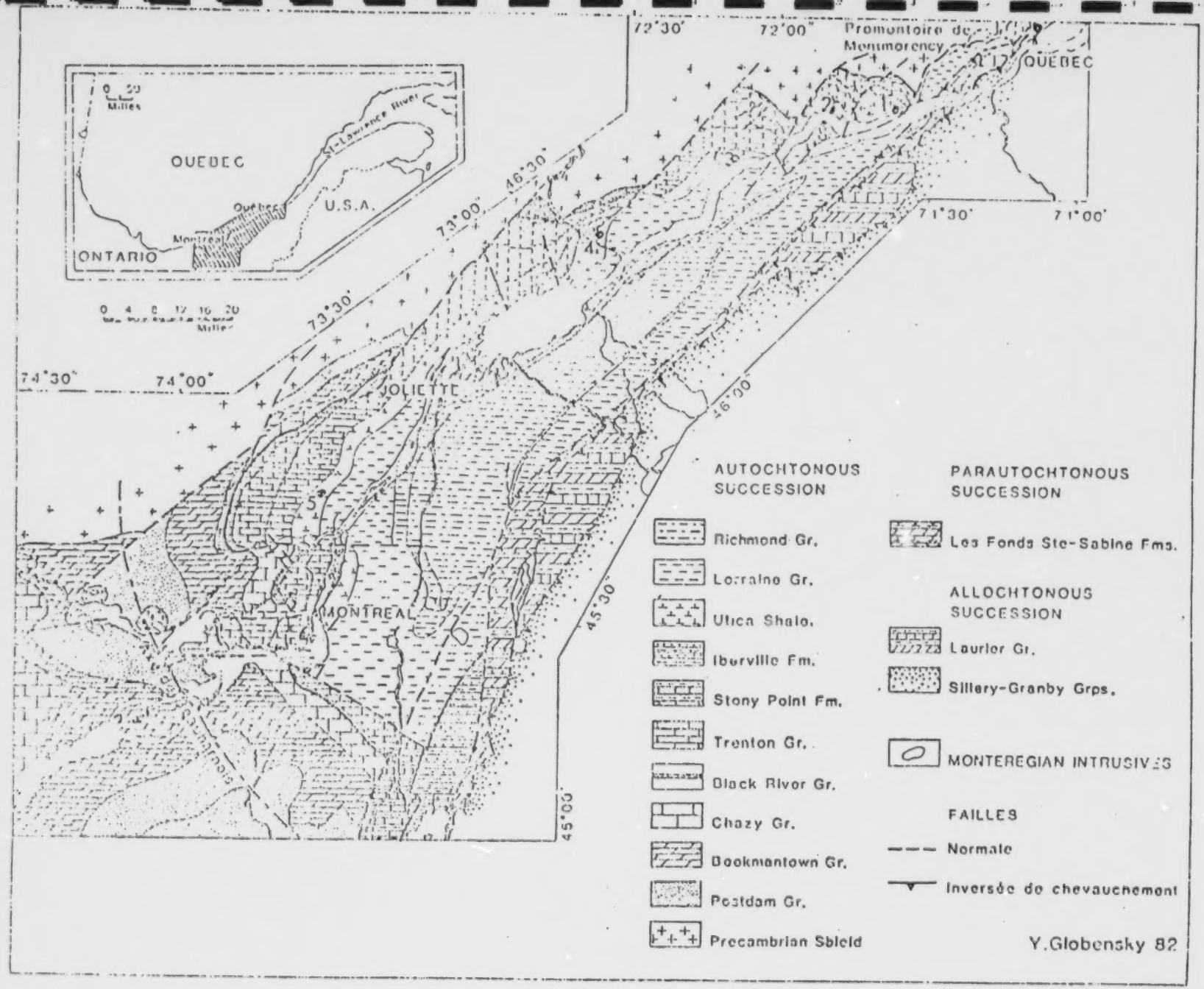


Figure 1 - Geological map of the St. Lawrence Lowlands of Quebec SW of Quebec City

APPENDIX 9-3

IGT THERMOBALANCE

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

NEW BRUNSWICK RESEARCH AND PRODUCTIVITY COUNCIL HYDRORETORTING TESTS

FINAL REPORT

IGT PROJECT 40913

Prepared for

HYCRUDE CORPORATION

November, 1982

Introduction

When conventional retorting processes are applied to the hydrogen-deficient oil shales (such as the Devonian - and Mississippian-age oil shales) a large fraction of the organic carbon content is left unconverted in the form of coke in the spent shale. By hydrogen retorting at elevated pressures, it has been possible to recover up to 90% of the organic carbon in these shales as useful products. These yield improvements have been achieved with both U.S. oil shales and those from various other countries.

The objective of this program is to determine, through a laboratory thermobalance test, whether high yields can be achieved by hydroretorting the oil shale of interest to the New Brunswick Research and Productivity Council (NBRPC). This report presents the results of the thermobalance and Fischer Assay tests conducted on composites of the NBRPC oil shale supplied to IGT. All analytical as well as test data are included in this report. Chemical analyses have been performed on spent shale from the Fischer Assay as well as the hydroretorting spent shale.

Thermobalance Test Procedure

These experiments investigated the hydroretorting behavior of the NBRPC oil shale as a function of time and temperature at a constant pressure. The rate of organic carbon conversion to gaseous products are measured. In the thermobalance, the shale sample is continuously weighed as the sample undergoes a programmed temperature sequence. The amount of unconverted organic material is determined by a chemical analysis of the spent shale after each run.

The thermobalance and related apparatus are shown in Figure 1. Conventional feed gas supply, control and preheat equipment are used. The gas rates to the different sections of the reactor are adjusted by use of rotameters; the total flow through the reactor is measured at the reactor exit with a dry test meter. The conditions used for the test of the NBRPC oil shale were 500 psig H_2, a 20°F/min heat up rate, a maximum temperature of 1400°F, and a 10 min hold at 1400°F. In this test, the power input was automatically adjusted to give a constant heat up rate to 1400°F and to hold the temperature at 1400°F for 10 minutes.

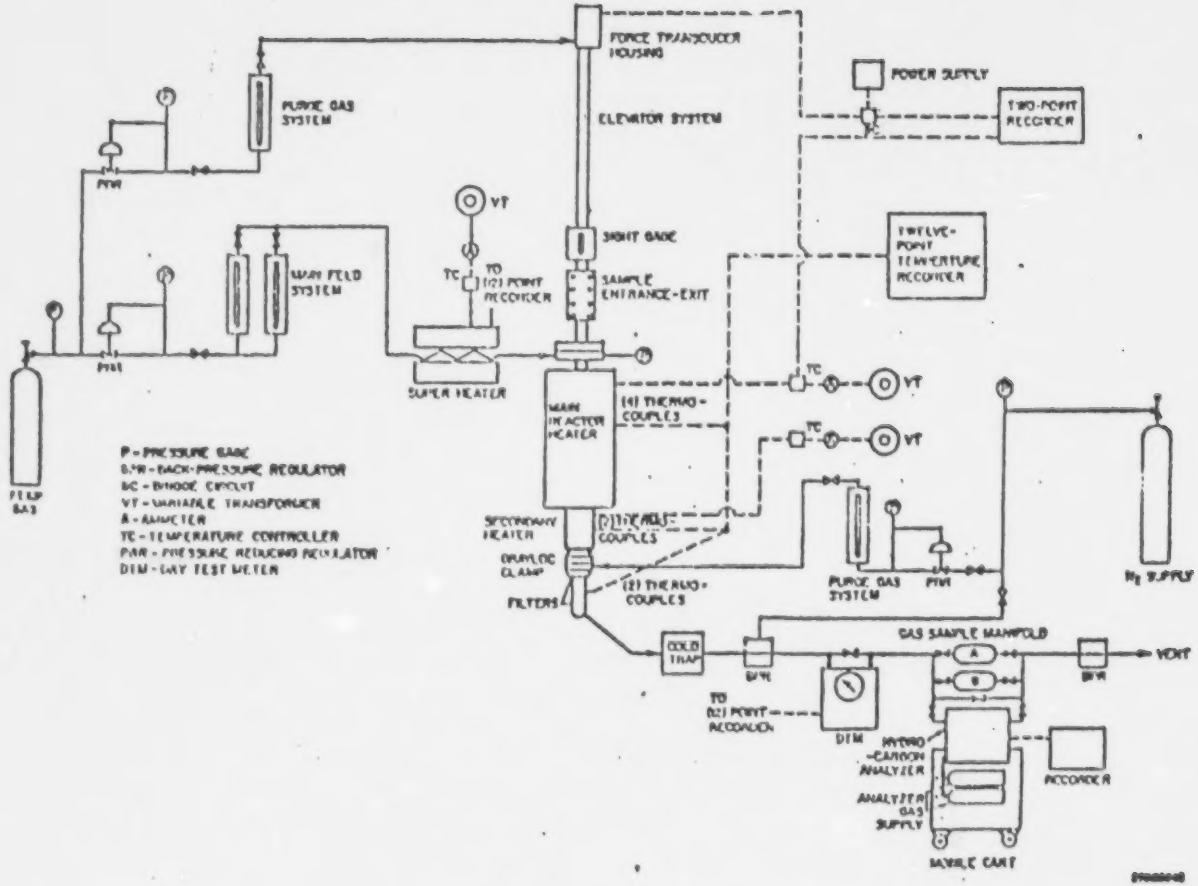


Figure 1. FLOW DIAGRAM FOR THERMOBALANCE UNIT

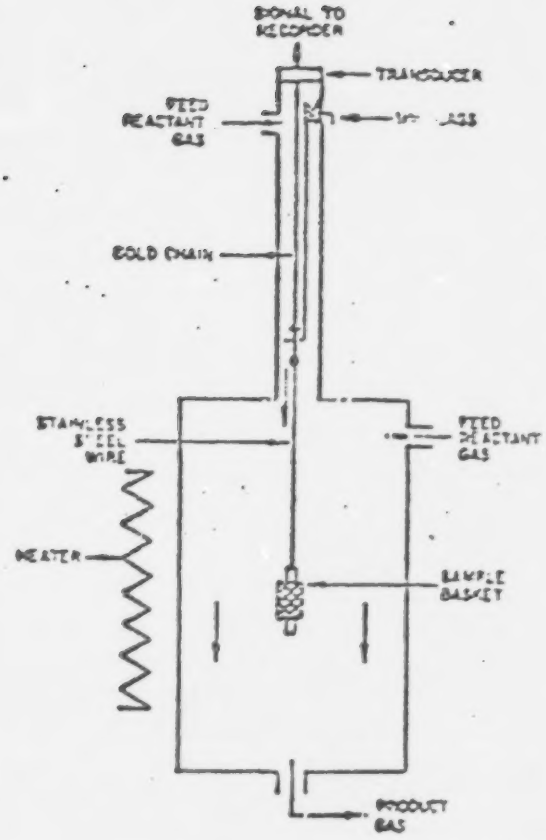


Figure 2. SCHEMATIC DIAGRAM OF IGT THERMOBALANCE REACTOR

The thermobalance reactor is made of type RA 330 steel and is designed to operate at pressures up to 1000 psig and temperatures up to 1500°F. Figure 2 shows the basic components of the weighing system. The sample is raised or lowered by an externally operated windlass. When completely lowered, the sample hangs from a lever or balance arm that transmits the weight to the transducer. The transducer capacity is 100 grams. In this work, the shale sample weighed about 12 grams and the basket holding the sample was of a comparable weight. Weight changes of the order of 0.01 gram can be readily detected.

The original shale was sieved to obtain the fraction between 6 to 20 U.S.S. sieve sizes. This fraction was then riffled to obtain a sample of uniform composition. A riffled sample was also chemically analyzed.

In thermobalance tests, the shale sample is put in a stainless-steel wire screen basket measuring 3/8 inch in diameter and 3 inches in height. The reactor section is brought to the desired initial temperature with a steady gas flow of 20 SCF/hr. The sample is lowered into the reactor, and the power into the heating elements is automatically adjusted to achieve the desired time-temperature profile.

The shale sample is weighed before and after each run, and the residue is analyzed for carbon, carbonate, hydrogen, nitrogen, sulfur, and ash. During runs, the sample weight and the temperatures of four thermocouples surrounding the sample are continuously recorded along with the CO, CO_2 and light hydrocarbons in the exit gas stream.

Test Results

The NBRPC shale showed higher total carbon conversion as well as higher conversion of carbon to liquid under hydroretorting conditions than by Fischer Assay.

$$\frac{\text{Hydroretorting Total C Conversion}}{\text{Fischer Assay Total C Conversion}} : 1.84$$

$$\frac{\text{Hydroretorting Oil Yield}}{\text{Fischer Assay Oil Yield}} : 1.56$$

The total carbon conversion ratio is typical of values obtained in past work with Eastern U.S. oil shales. The oil yield ratio is also in the range of values for Eastern U.S. oil shales. Some Eastern U.S. oil shales, Kentucky and Indiana New Albany in particular, have somewhat higher oil yield ratios than were obtained for the NBRPC shale. This is probably reflective of a greater selectivity of organic carbon to liquid with New Albany shale than with the NBRPC shale tested. Because the total carbon conversion ratio is greater than the oil yield ratio, the additional carbon converted by hydroretorting has a lower selectivity to oil than the carbon converted by Fischer Assay. Western U.S. shales also have a lower oil yield ratio than the NBRPC shale tested.

The NBRPC shale has less mineral carbon than any shale tested by IGT, and this is reflected in the lower conversions of carbon to CO and CO_2 during hydroretorting. The total carbon conversion of the NBRPC shale under hydroretorting conditions is only several per cent lower than that of the New Albany (KY) shale studied extensively at IGT. However, the NBRPC shale shows a higher selectivity of carbon to gas under hydroretorting conditions and has a conversion of carbon to liquid 15 per cent lower than New Albany shale.

Composition	Proximate Analysis (wt %)		Ultimate Analysis (wt % dry)						
	Moisture	High Temperature H_2O	Ash	Total C	Organic C	Mineral C	Hydrogen	Sulfur	Nitrogen
Feed: NBRPC	2.16	3.97	82.86	10.52	10.48	0.03	1.27	2.47	0.38
Res: Fischer Assay	0	-	89.50	6.42	-	-	0.52	-	-
Res: NB-82-1	0.32	0.96	97.49	2.47	2.45	0.02	0.12	0.79	0.02

Fischer Assay

	C. Conv.	Conv Total C → gas[1]	Conv Total C → liq	Conv Org C → liq[2]	Oil Yield (gal/ton)
NBRPC	43.5.	6.4	37.1	37.2	11.5

Hydroretort	Total C Conv	Org. C Conv	Min. C Conv	Conv Total C → LHC[3]	Conv Total C → CO	Conv Total C → CO_2	Conv Total C → liq[4]	Conv Org. C → liq[2]	Oil Yield (gal/ton)
NB-82-1	80.2	80.3	43.2	21.95	0.15	0.1	58.0	58.2	18.0

1. By difference from total and liquid yields.
2. Assuming only organic carbon forms liquid.
3. Light hydrocarbon gases.
4. By difference from total, CO_x, and LHC yields.
5. Assuming oil from hydroretorting to have the same composition as Fischer Assay oil.

INSTITUTE OF GAS TECHNOLOGY
ANALYTICAL REPORT - MODIFIED FISCHER ASSAY
CHEMICAL AND PHYSICAL TESTING LABORATORY

ject No. 40913-00 Requested by Rue Lab No. 47651

mple New Brunswick Shale

Fischer Assay, Moisture-free Basis

Oil, wt.%.....	4.5
Water, wt.%.....	1.8
Spent Shale, wt.%.....	92.2
Gas + Loss, wt.%.....	1.5
Total...	100.0
Oil Yield, Gal/Ton.....	11.5
Water, Gal/Ton.....	4.3

isture, wt.% (Oven Dried) 2.29
oisture, wt.% (Air Dried).

Oil Phase Analysis

Sp Gr 60/60F.....	0.936
Ultimate Analysis	
Carbon, wt.%	84.76
Hydrogen, wt	10.52
Sulfur, wt.%	
Nitrogen, w %.....	
Ash, wt.%.....	0.3
C/H Weight Ratio.....	8.06

Shale Analysis, Moisture-free

Carbon, Organic, wt.%...	
Hydrogen, wt.%.....	
Sulfur, wt.%.....	
Nitrogen, wt.%.....	
Ash, Corrected, wt.%....	
Carbon Dioxide, wt.%....	

isture, wt.% (Ground).....

Spent Shale Analysis, Moisture-free

Carbon, ~~Organic~~ Total, wt.%....	6.42
Hydrogen, wt.%.....	0.52
Sulfur, wt.%.....	
Nitrogen, wt.%.....	
Ash, Corrected, wt.%.....	89.50
Carbon Dioxide, wt.%.....	

Moisture, wt.% (Ground)..... 0.00

tes 10 cc/min argon purge used

alyst KP, MP, SJ

te 11-15-82

Supervisor

APPENDIX 9-4

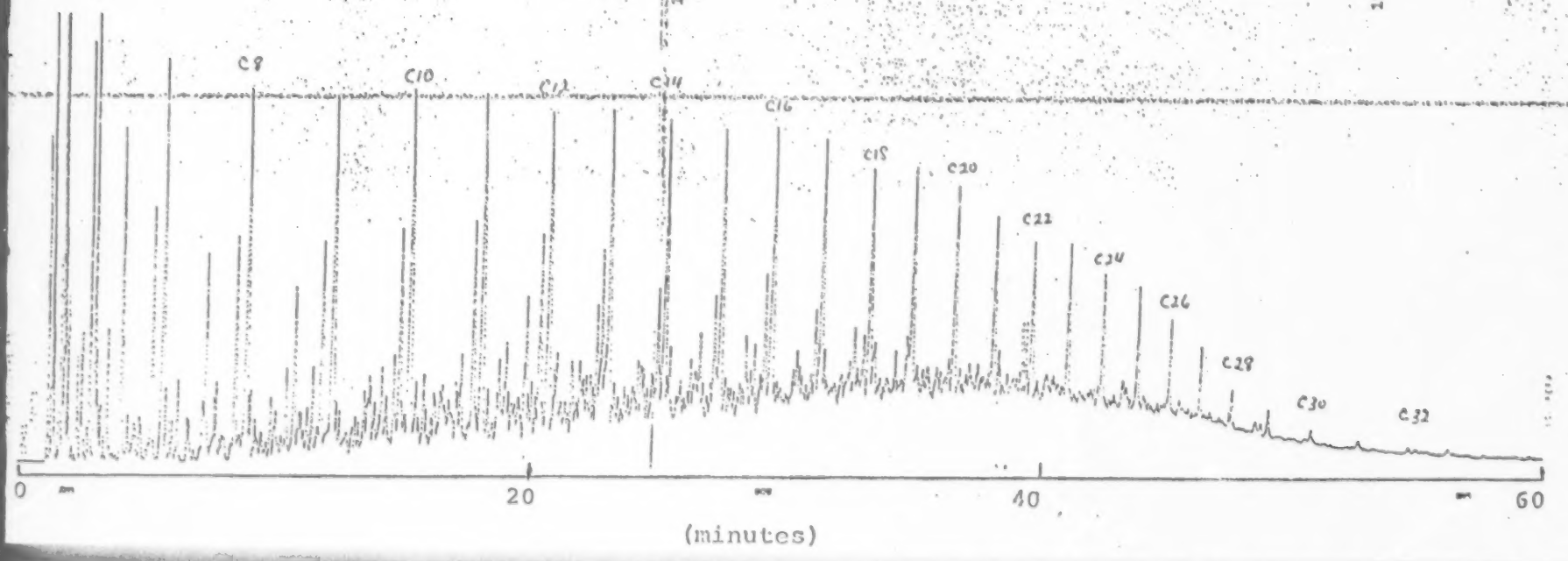
GAS CHROMATOGRAMS OF LIQUID PRODUCTS

9.4 GAS CHROMATOGRAPHY OF LIQUID PRODUCTS

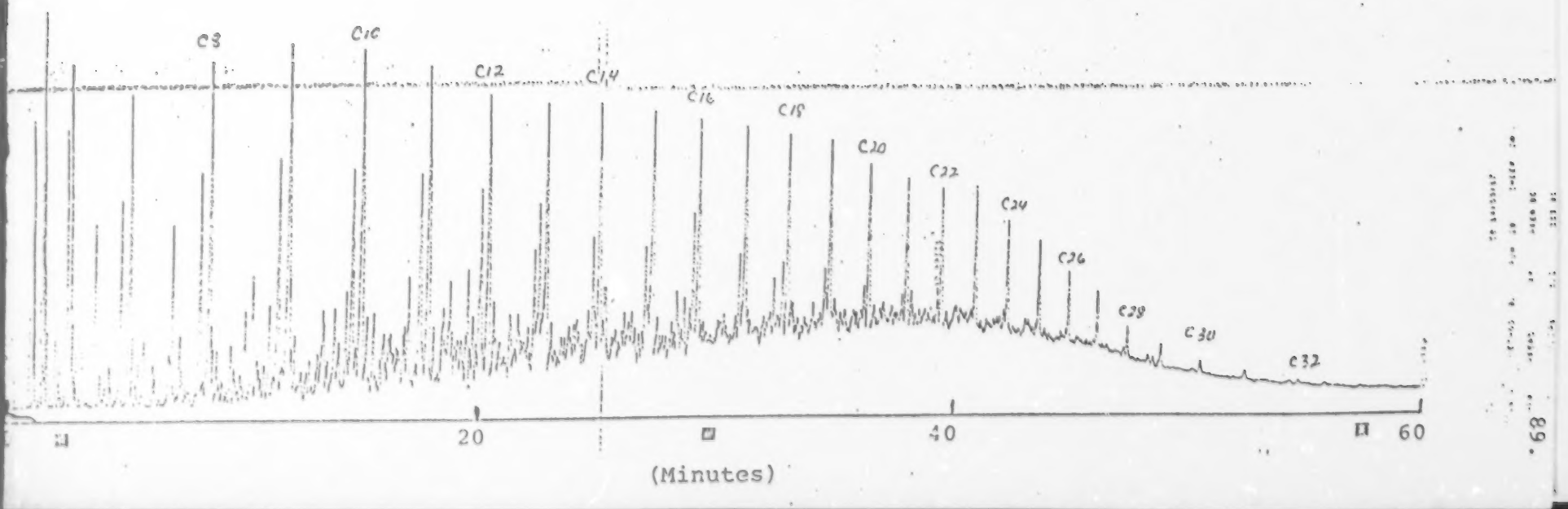
The liquid products from the retorting tests were analysed by capillary gas chromatography. Analyses were performed using a Varian 6000 gas chromatograph equipped with a 50 m x 0.316 mm DB-1 Fused Silica column and a flame ionization detector. The following parameters were used:

Sample size	-	0.25 µl
Oven temperature	-	40°C for 4 minutes, 40°C to 300°C at 5°C/minute, 300°C for 15 minutes
Carrier gas	-	He, 80 psi, Column 2.38 ml/min Make up 30 m/min
Detector	-	H_2 42 psi, 30 ml/min Air 58 psi, 300 ml/min
Injector temperature	-	325°C
Detector temperature	-	325°C
Senstitivity	-	32×10^{-10}
Chart speed	-	1 cm/min

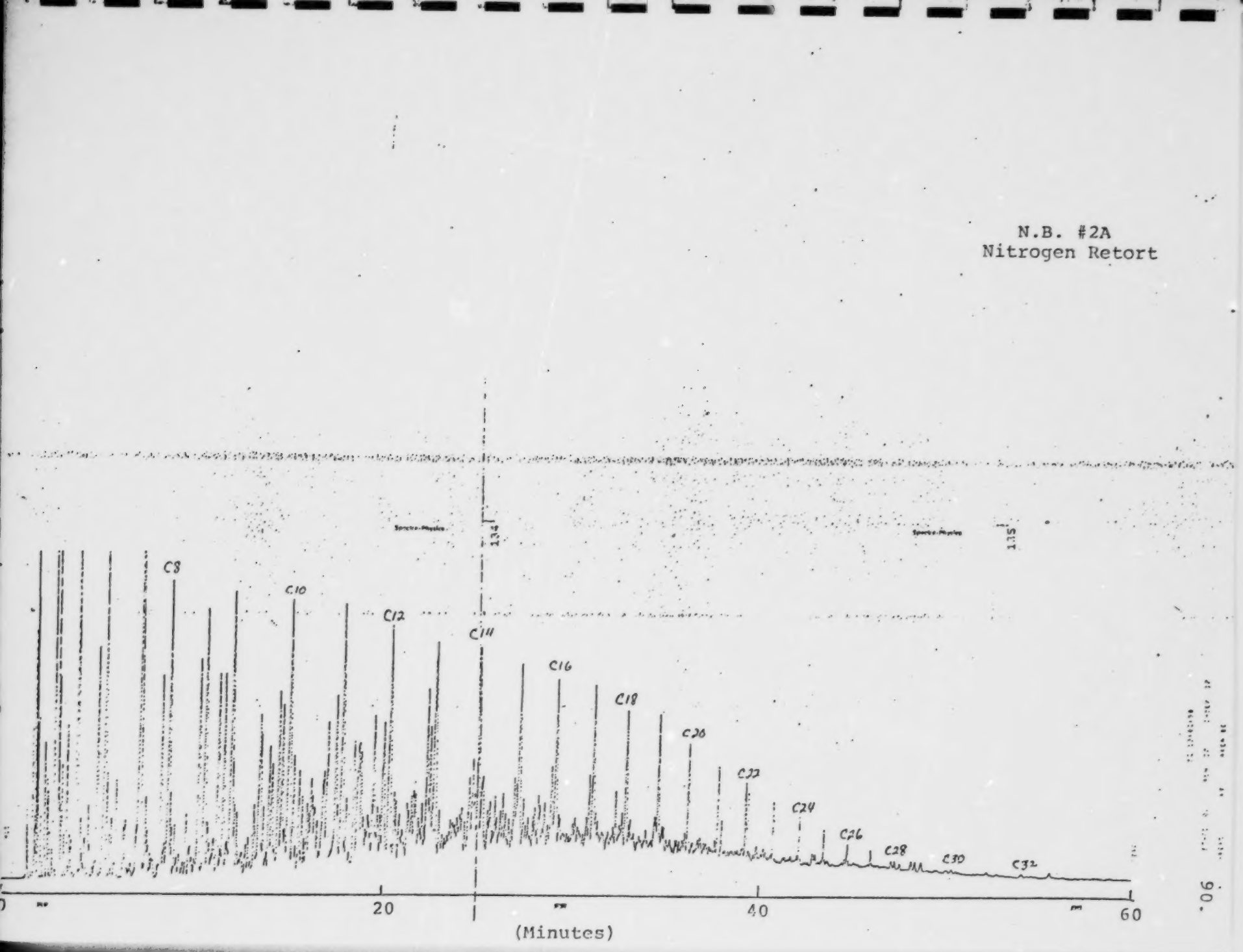
N.B. #1
Hydrogen Retort



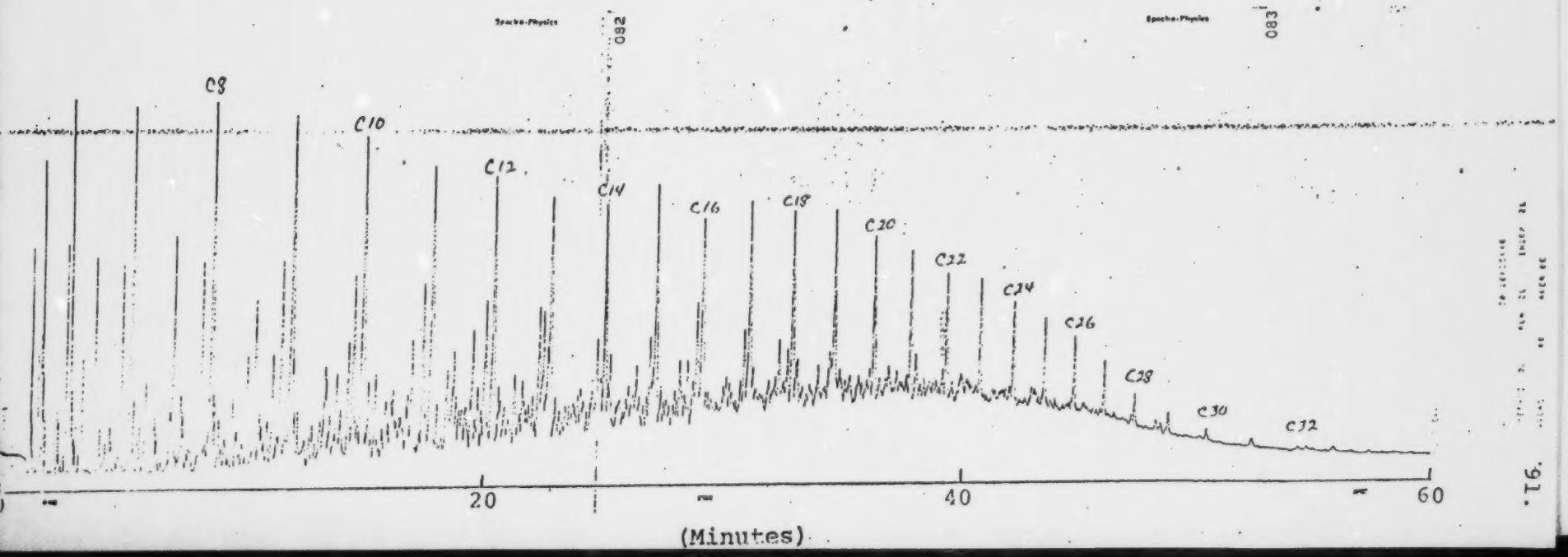
N.B. #2a
Hydrogen Retort



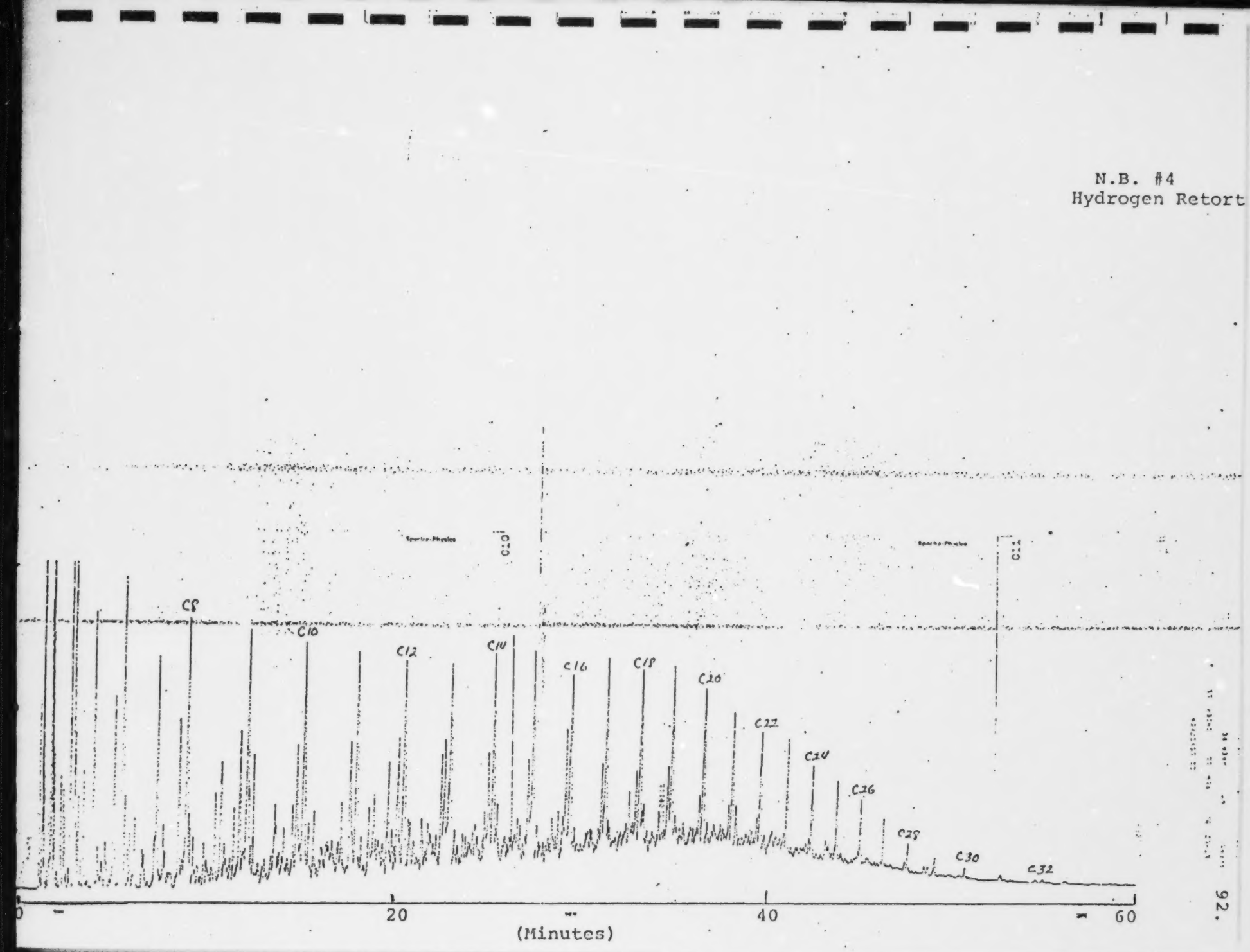
N.B. #2A
Nitrogen Retort



N.B. #3
Hydrogen Retort

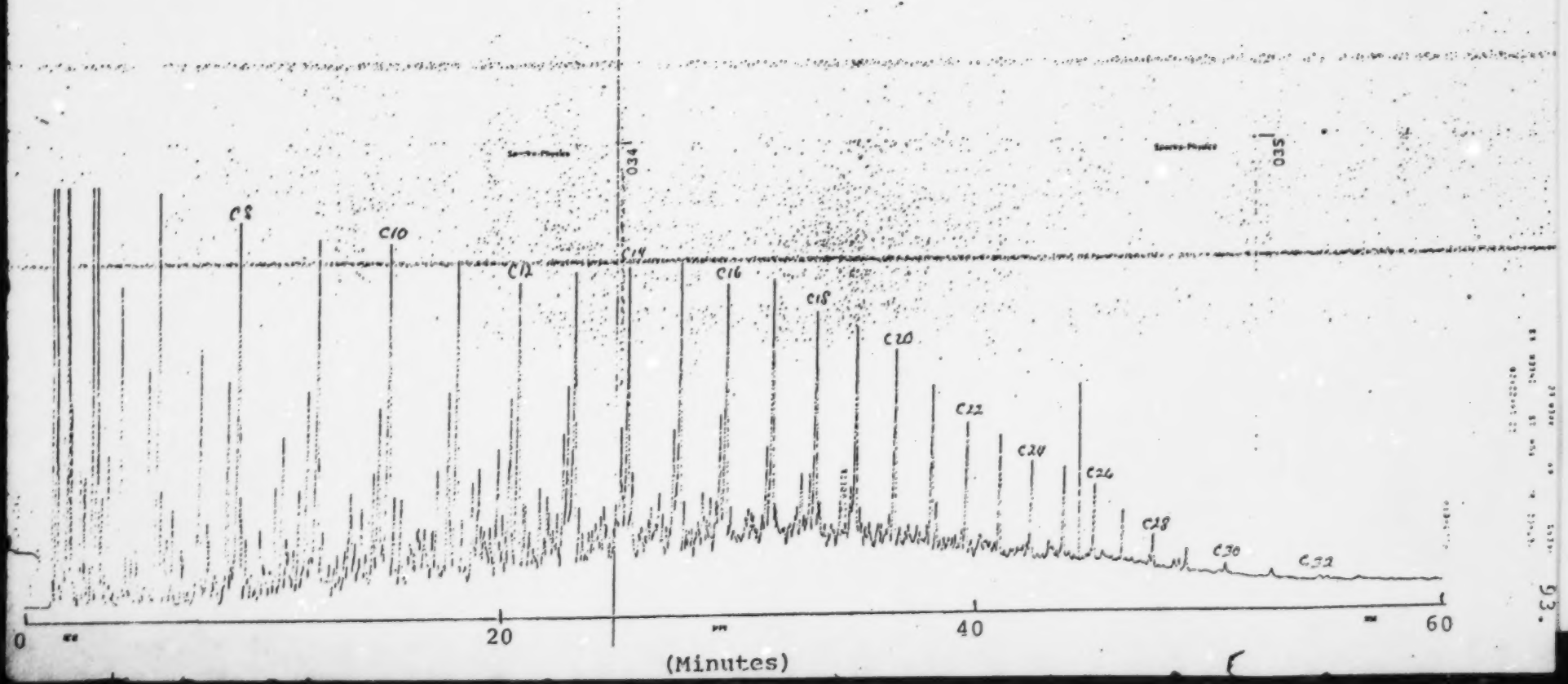


N.B. #4
Hydrogen Retort

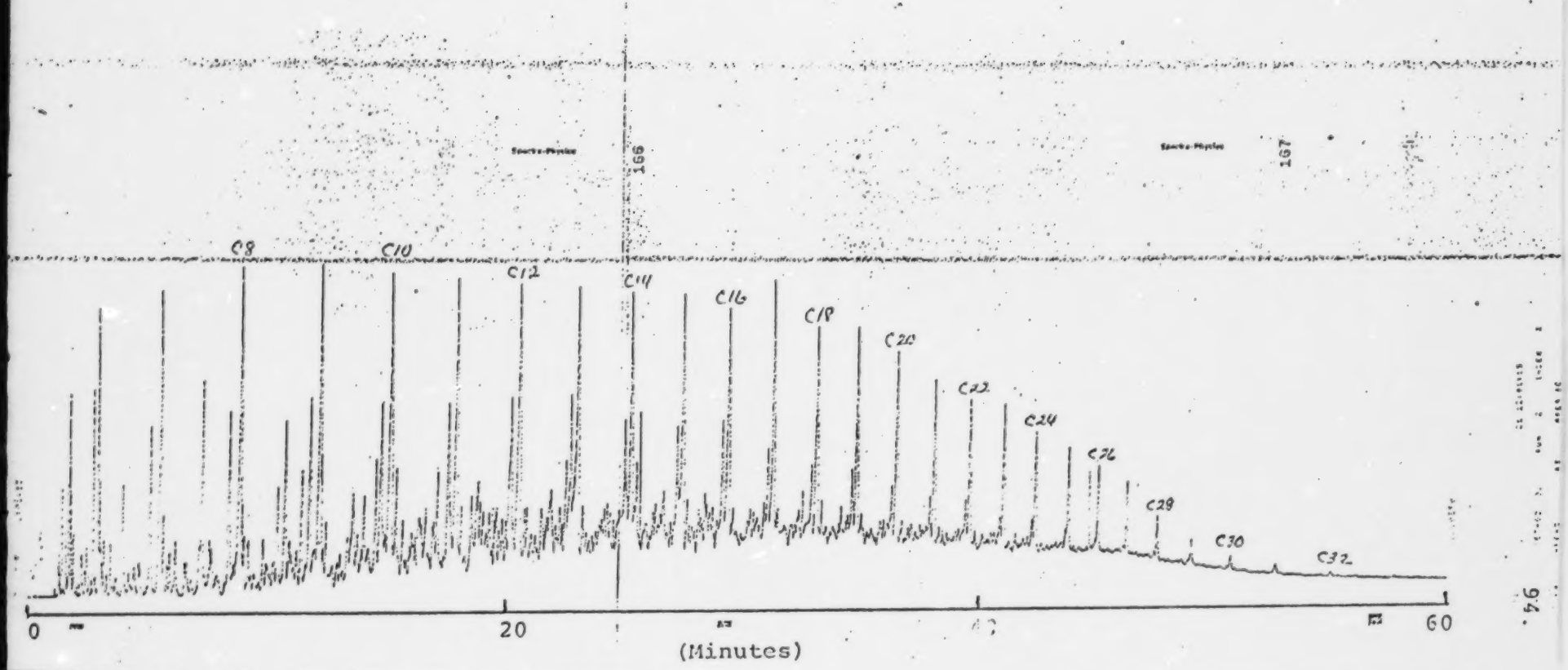


92.

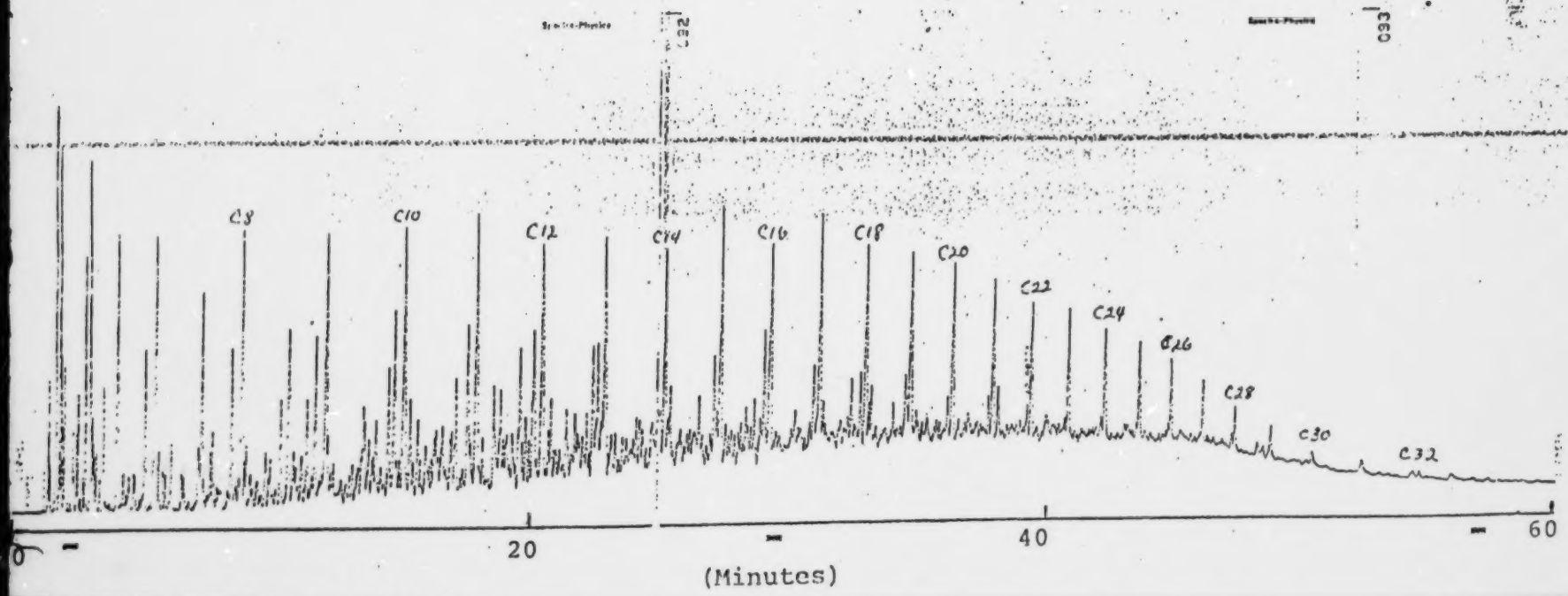
N.B. #5
Hydrogen Retort



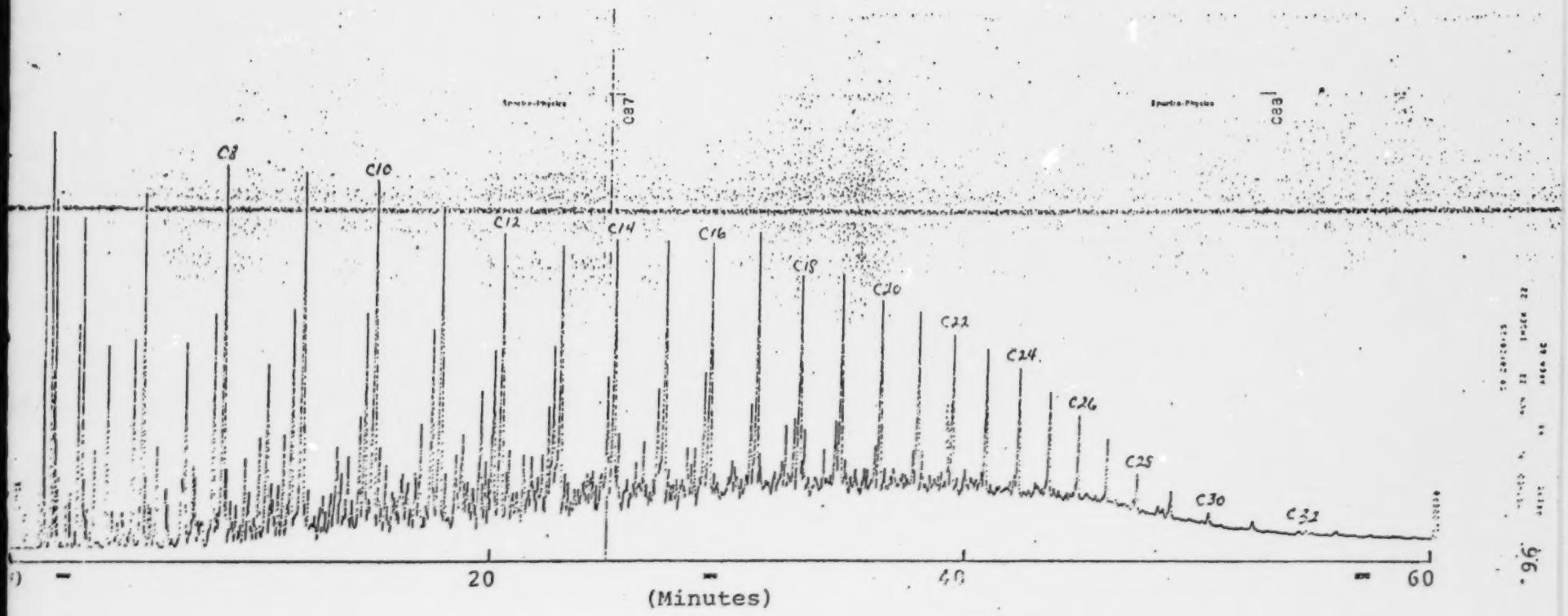
N.B. #5
Nitrogen Retort



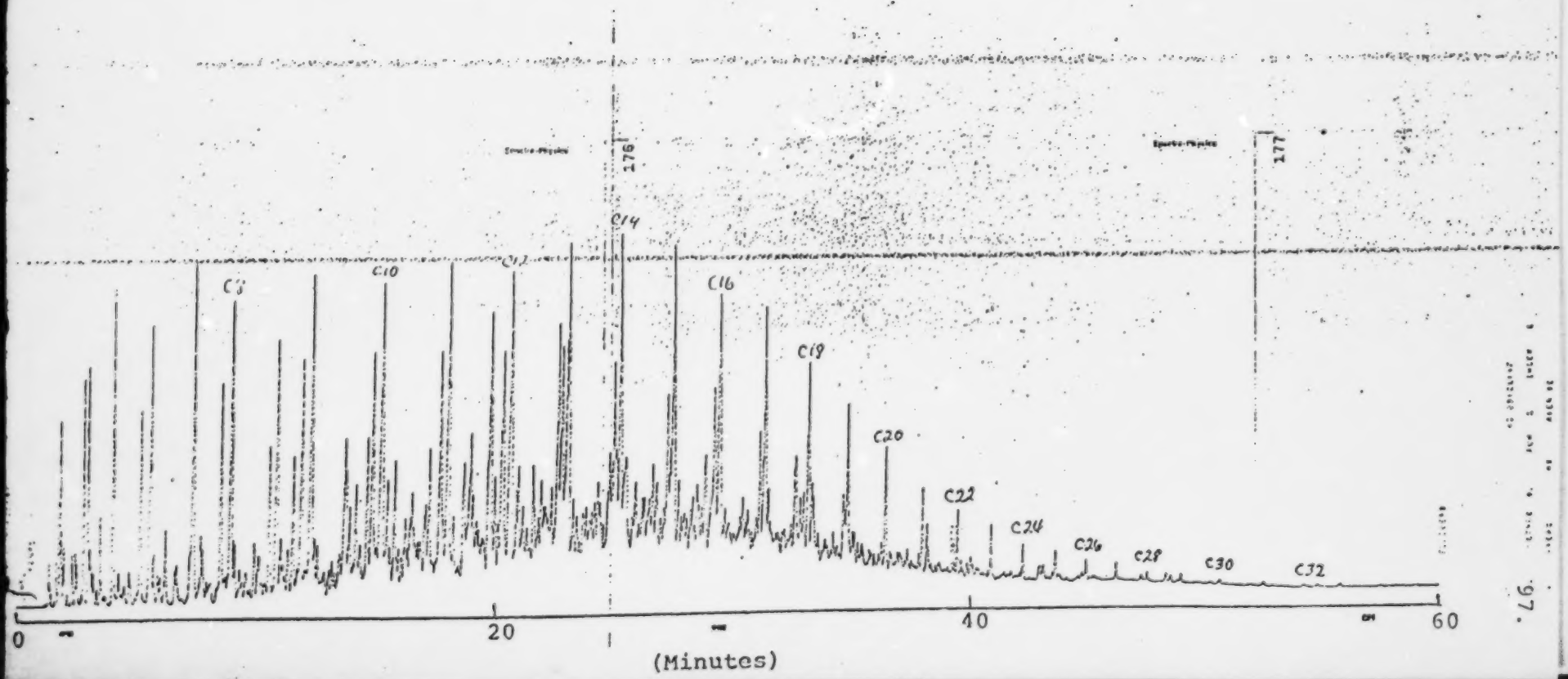
N.B. #6
Hydrogen Retort



N.B. #7
Hydrogen Retort

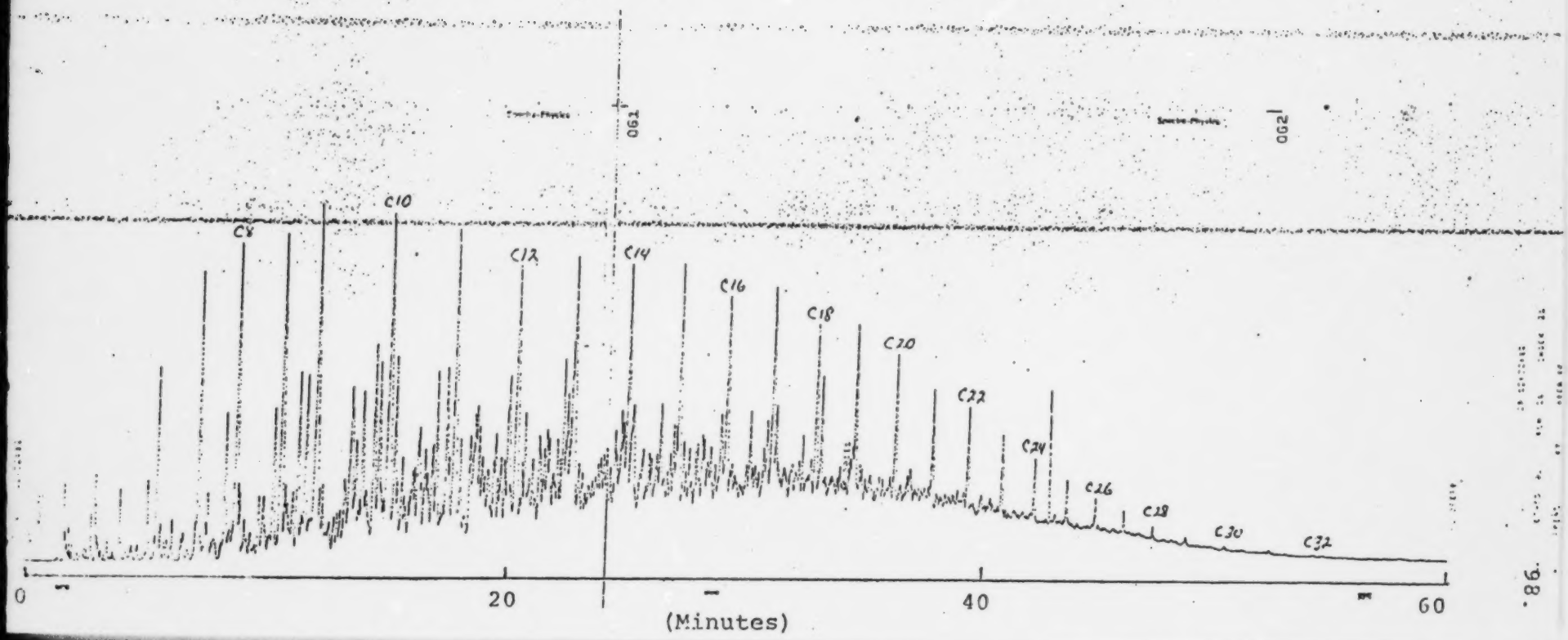


N.B. #8
Hydrogen Retort

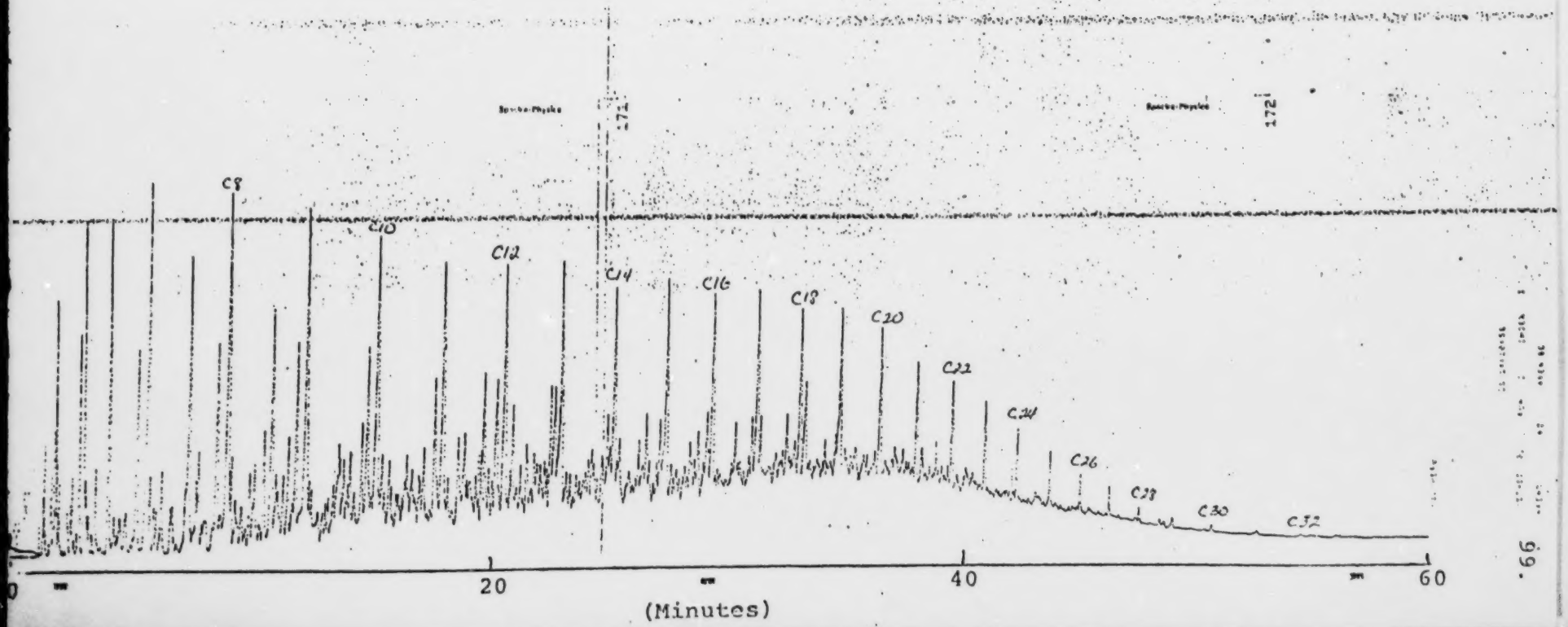


97.

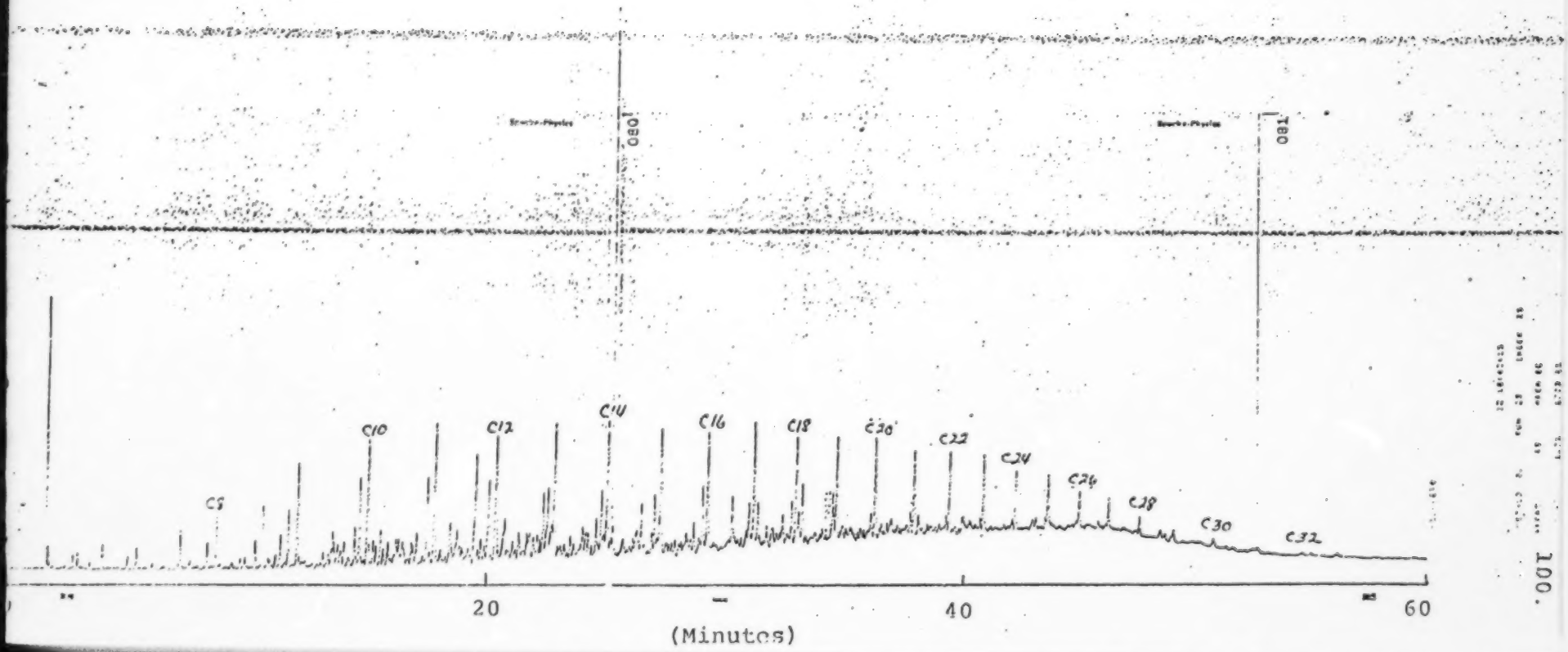
N.B. #9
Nitrogen Retort



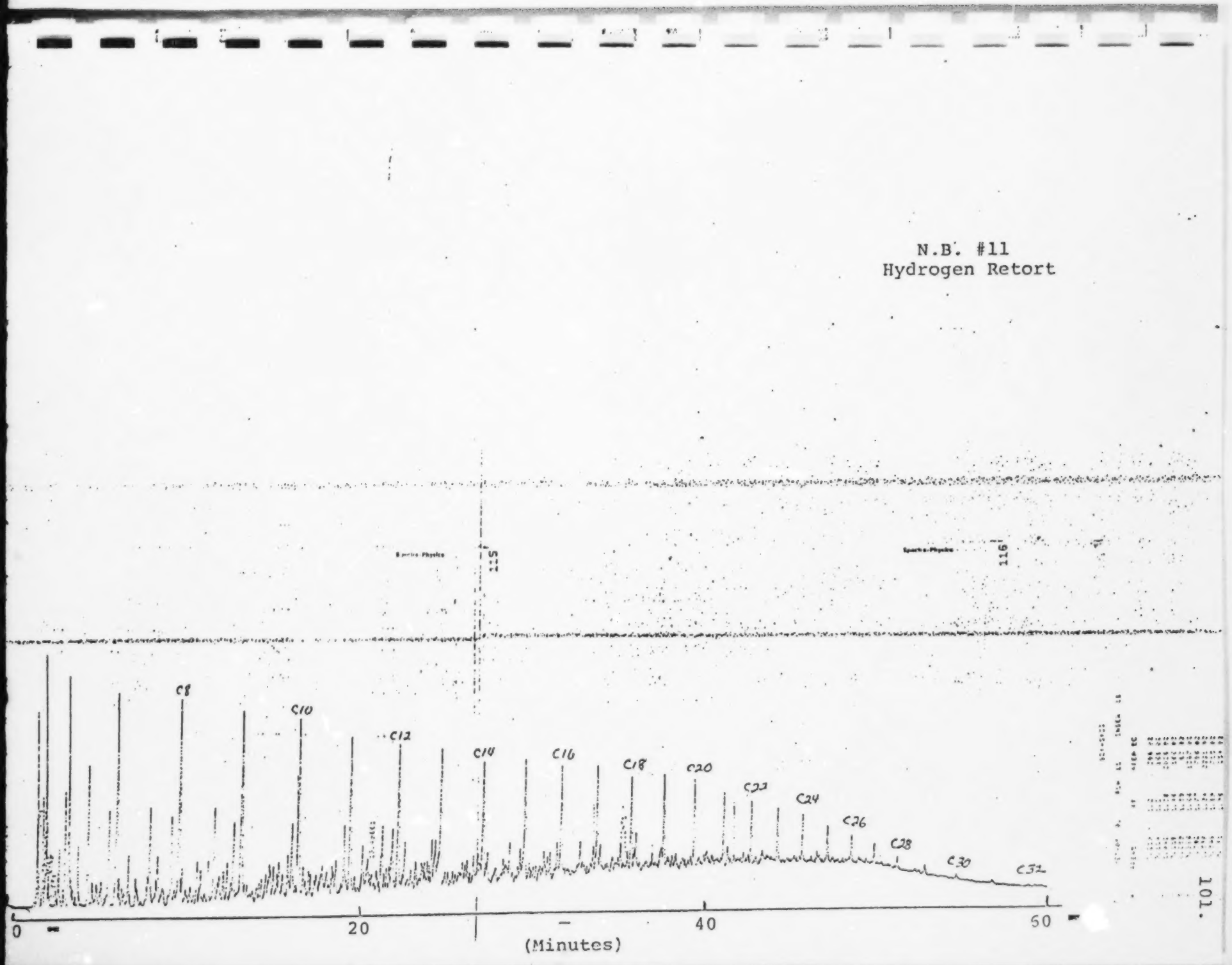
N.B. #9
Hydrogen Retort



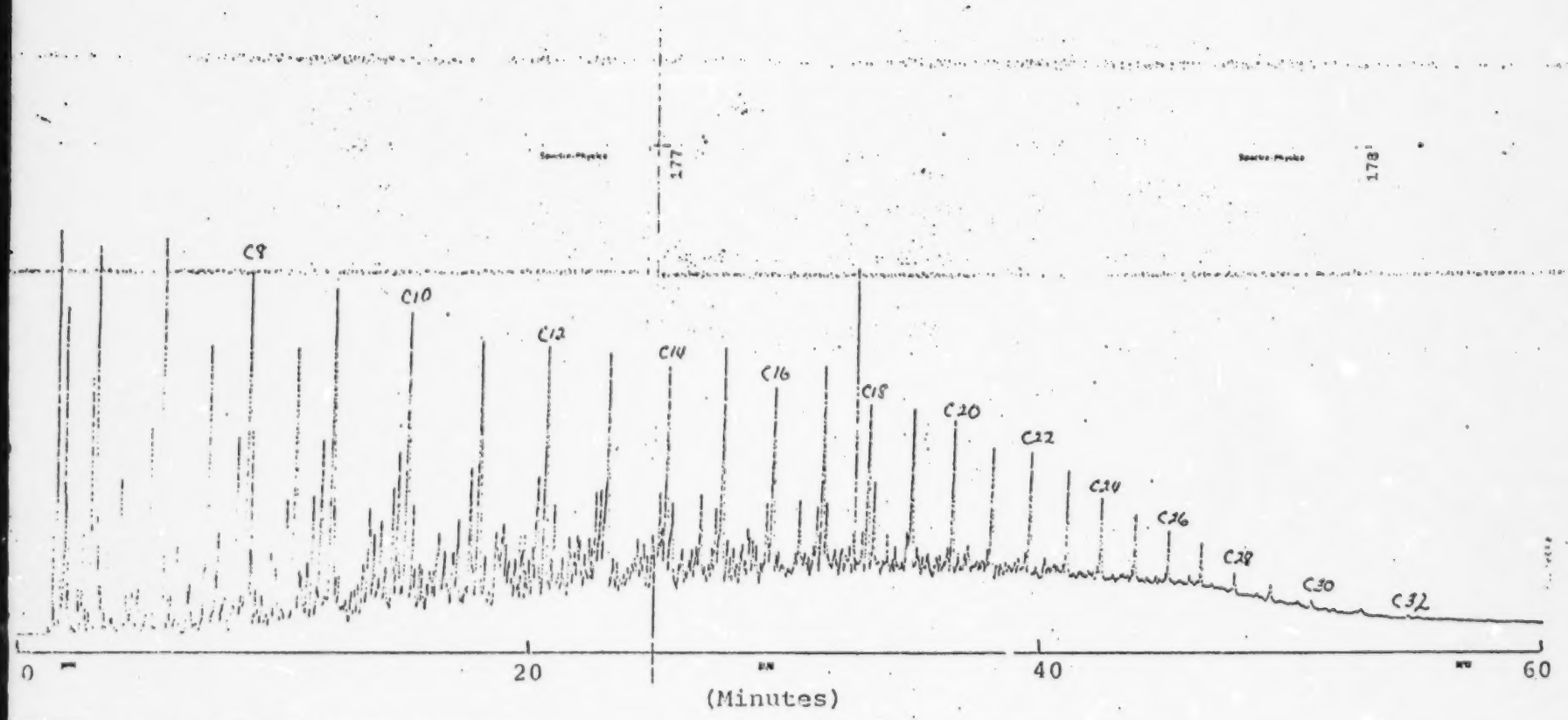
N.B. #10
Hydrogen Retort



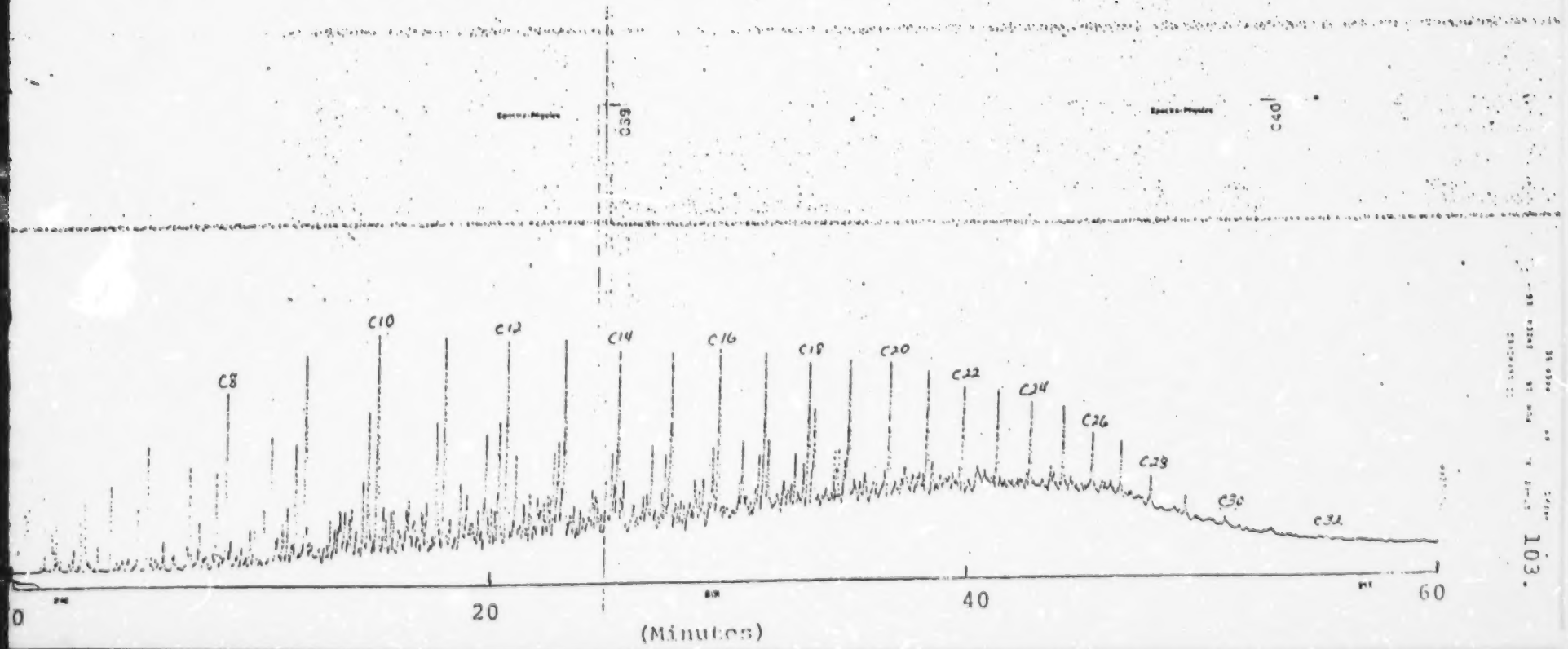
N.B. #11
Hydrogen Retort



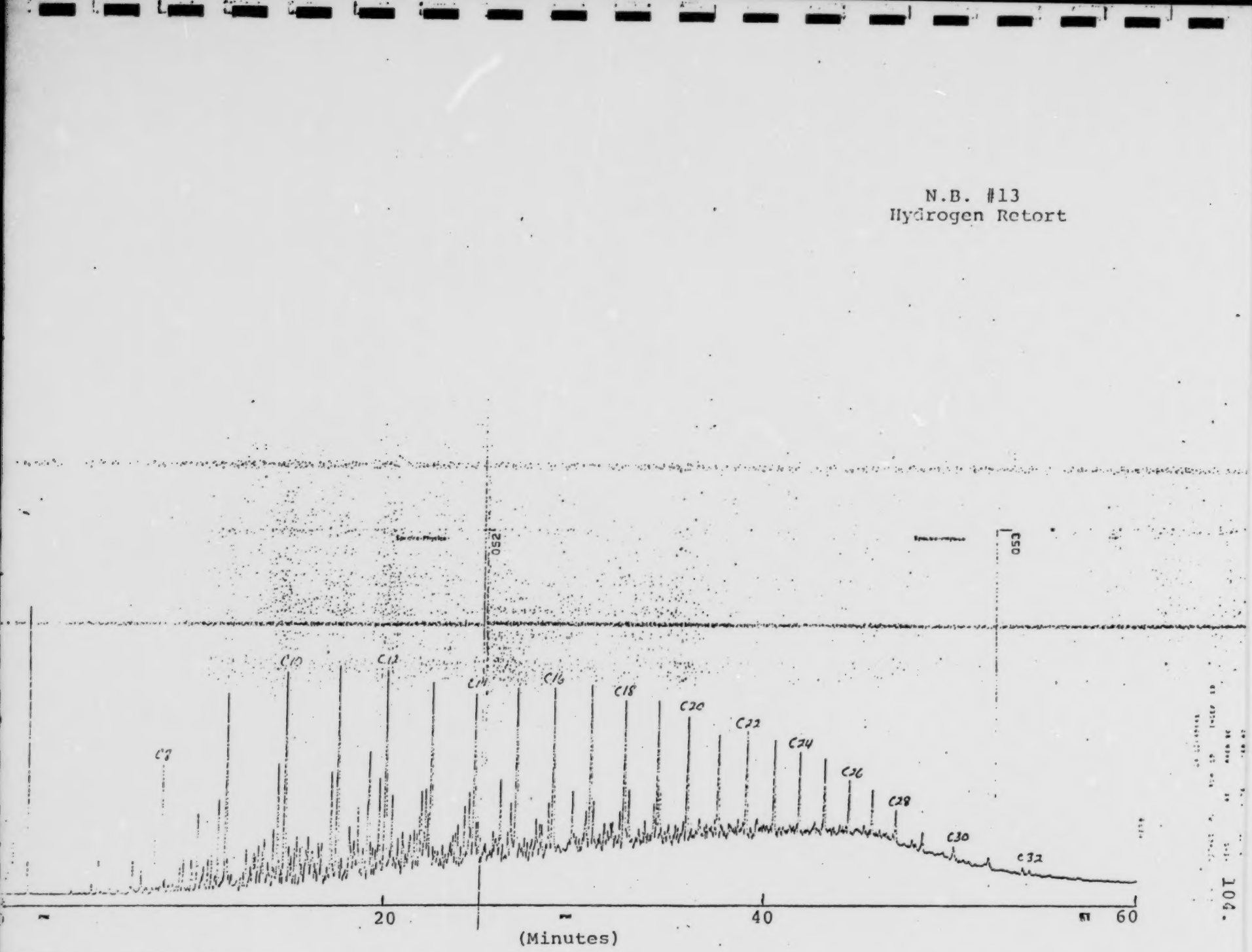
N.B. #11
Nitrogen Retort



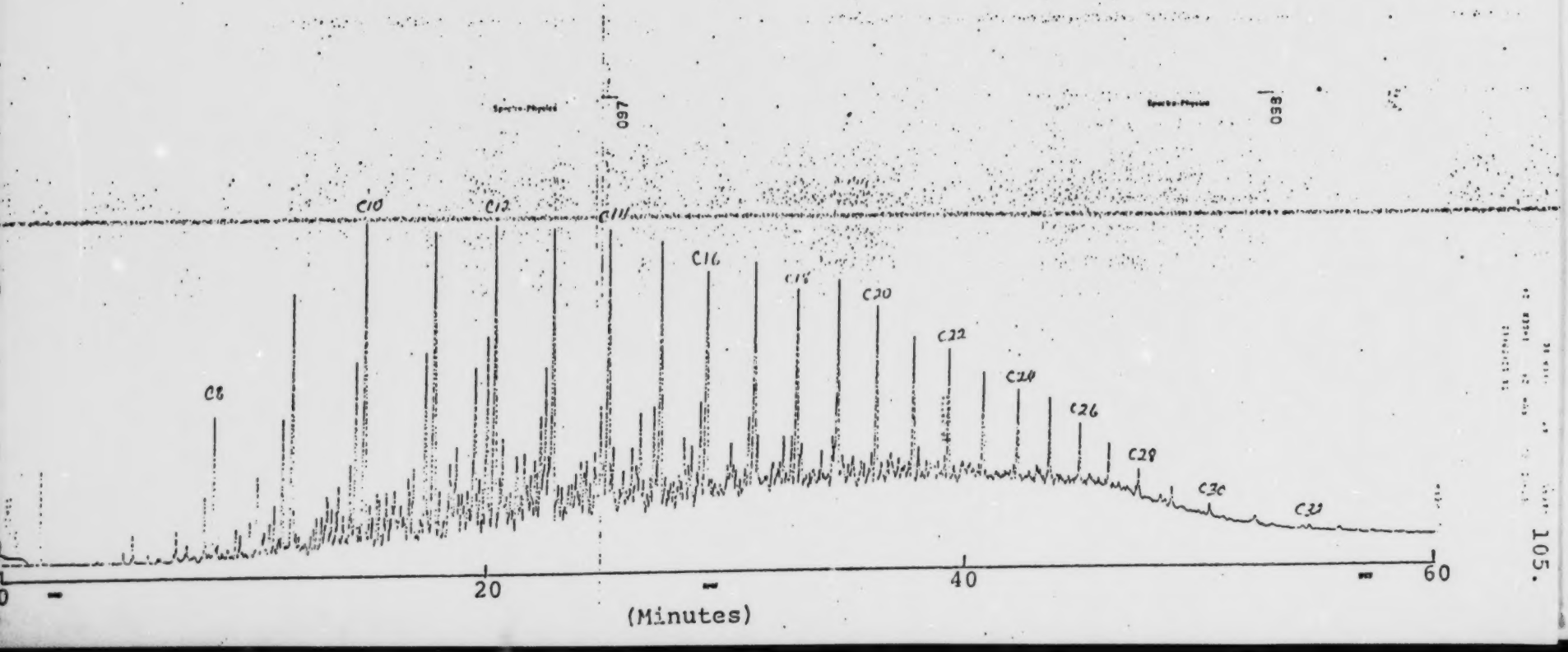
N.B. #12
Hydrogen Retort



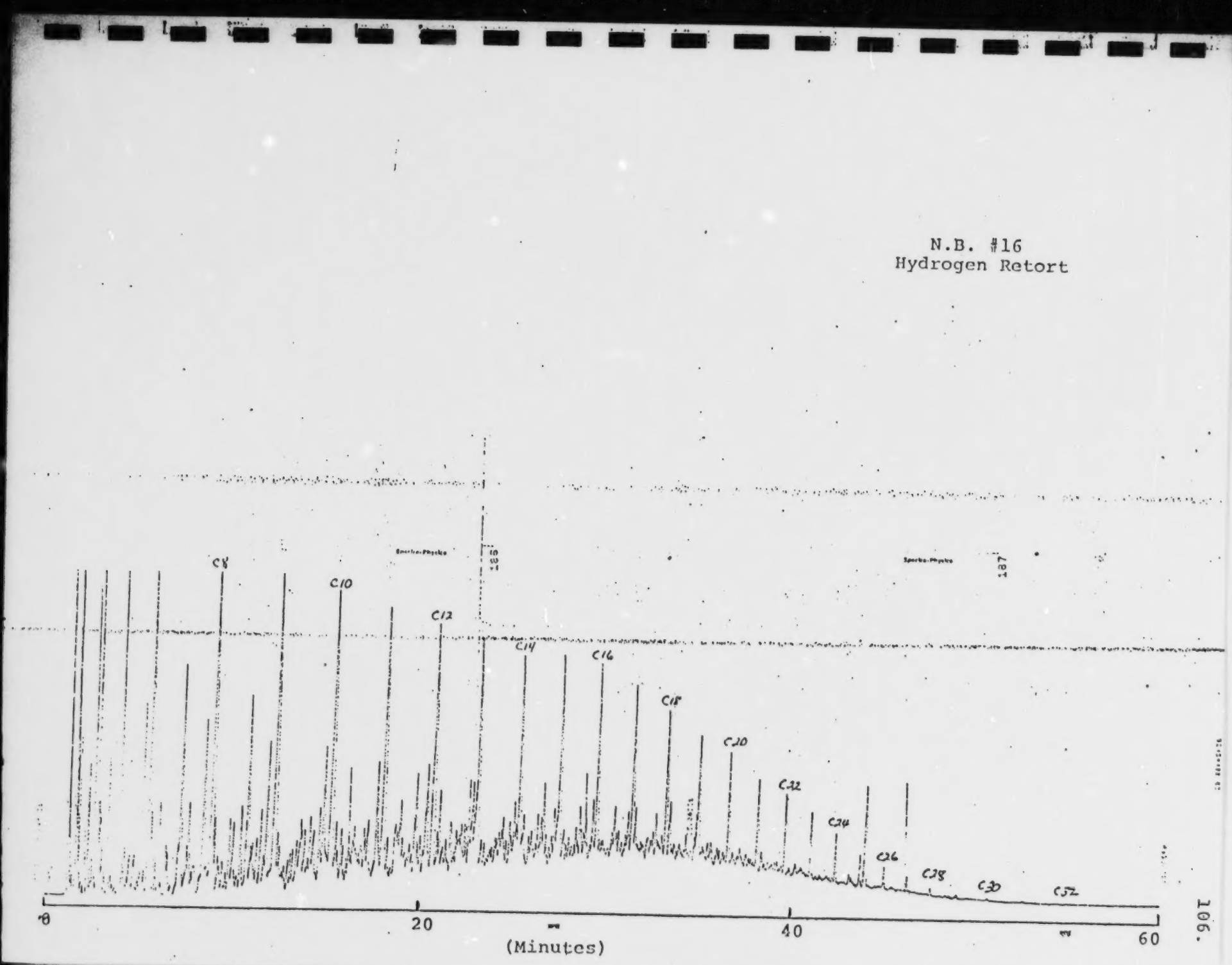
N.B. #13
Hydrogen Retort



N.B. #14
Hydrogen Retort

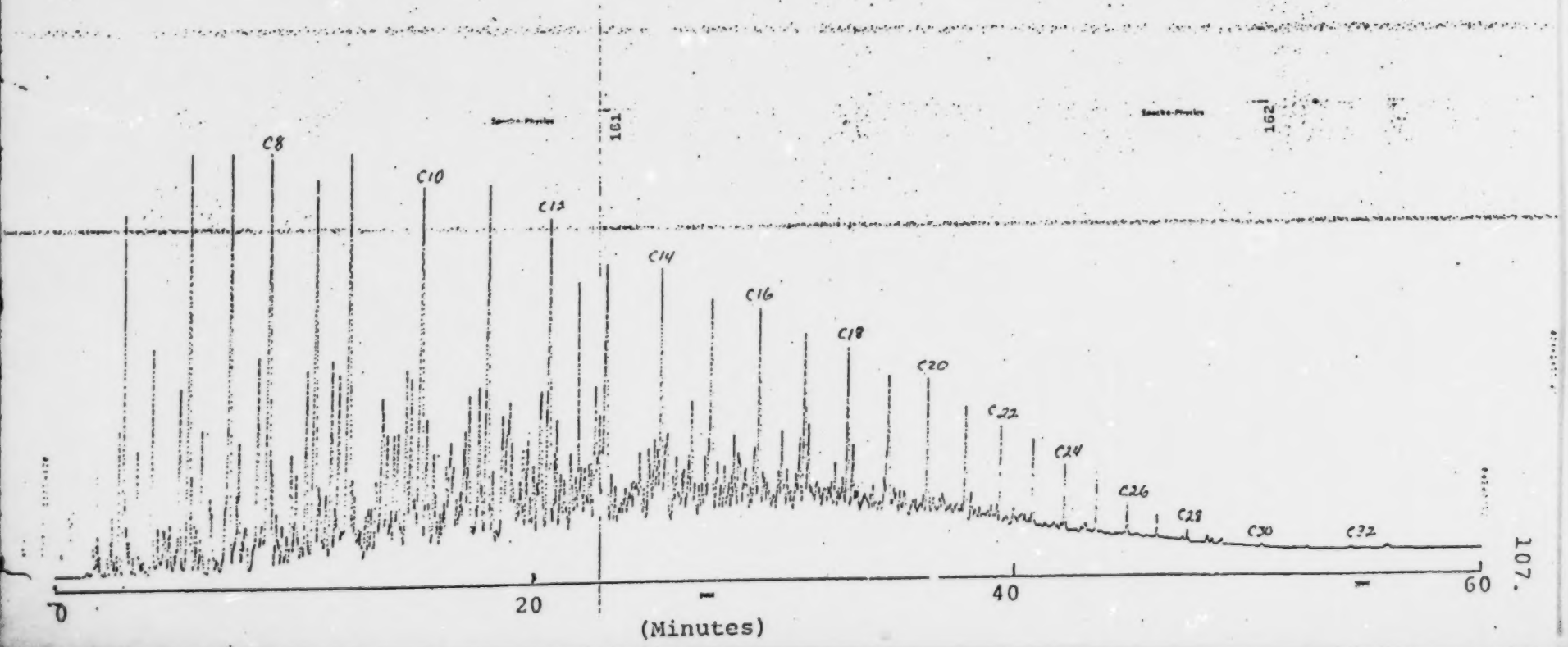


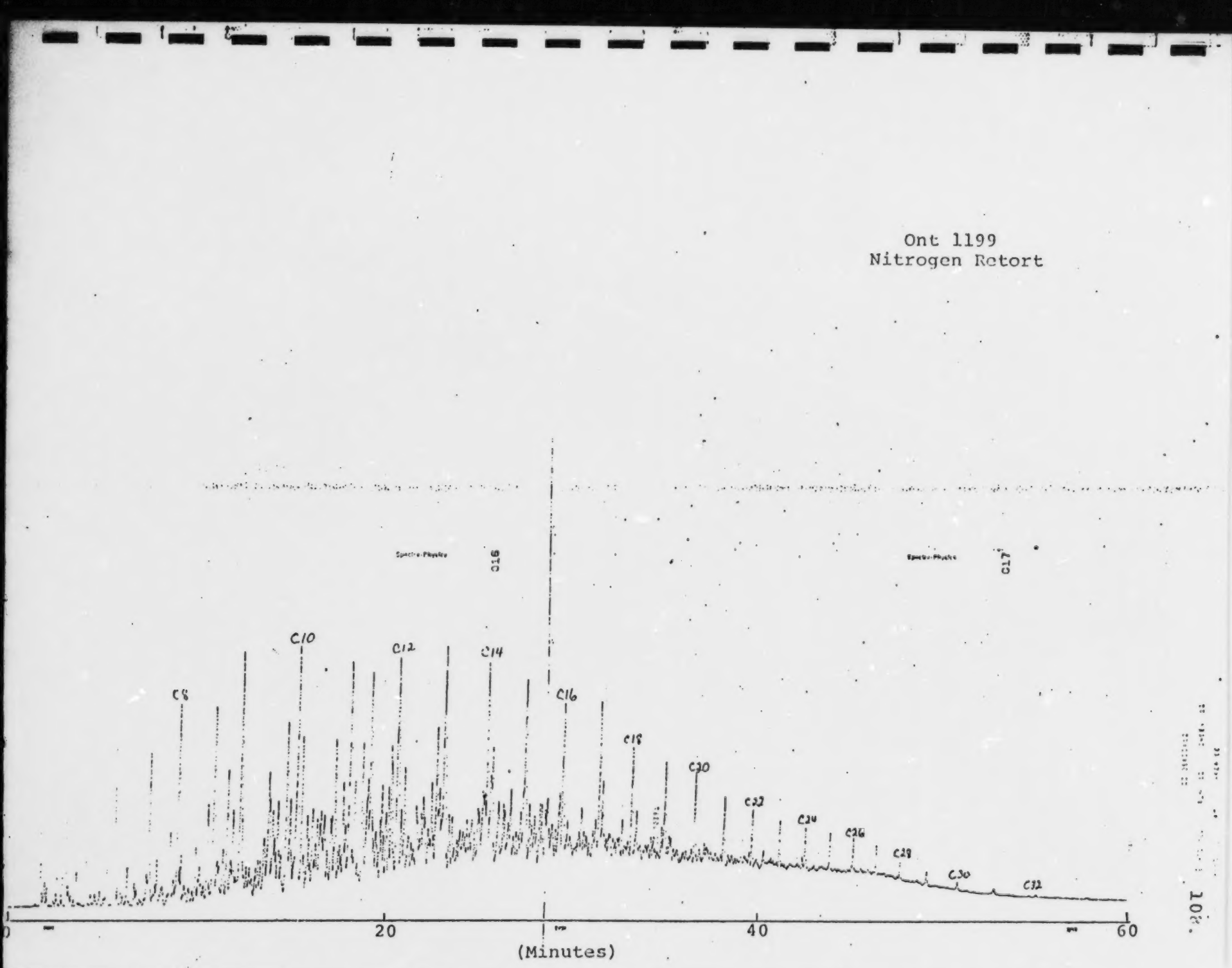
N.B. #16
Hydrogen Retort



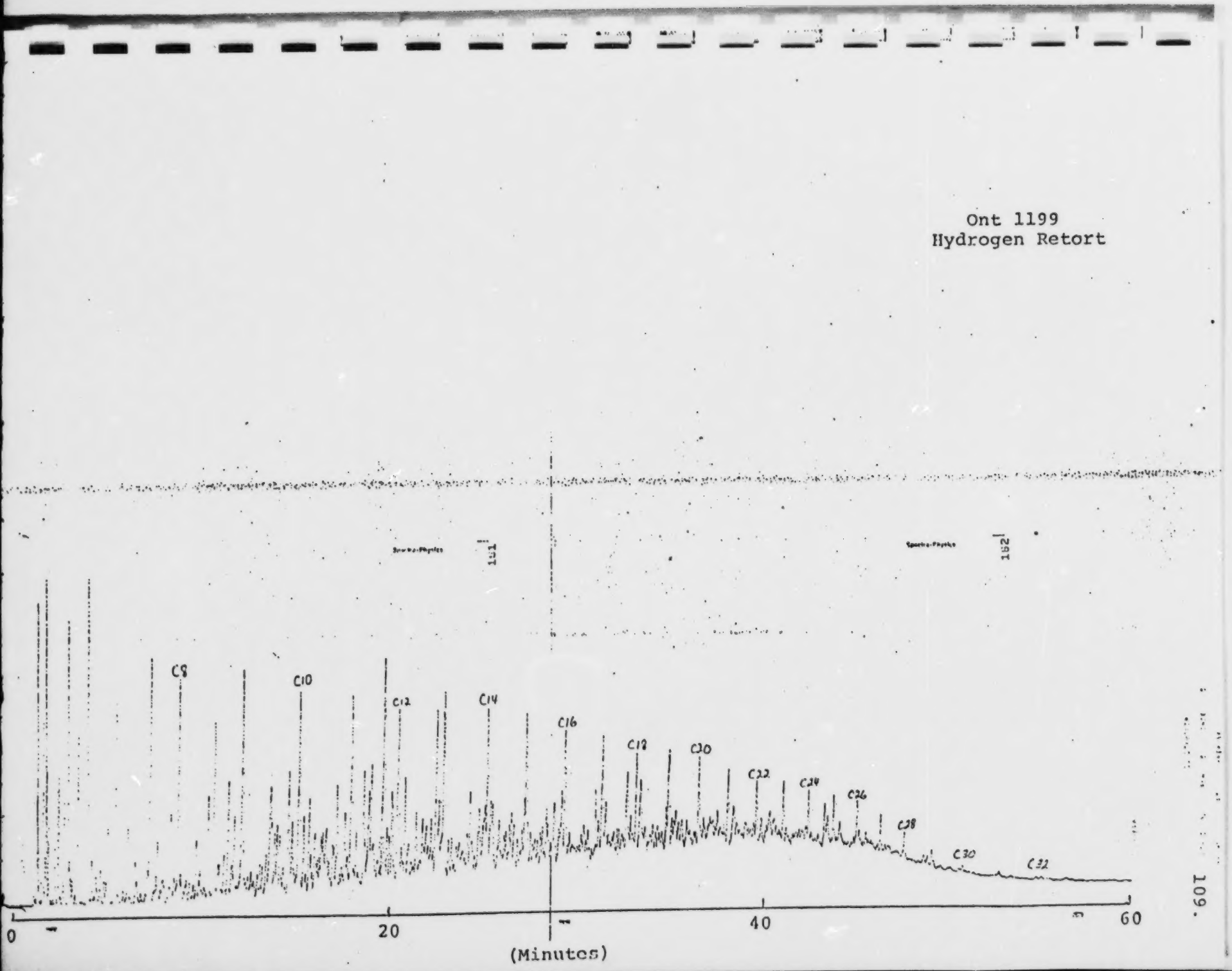
106.

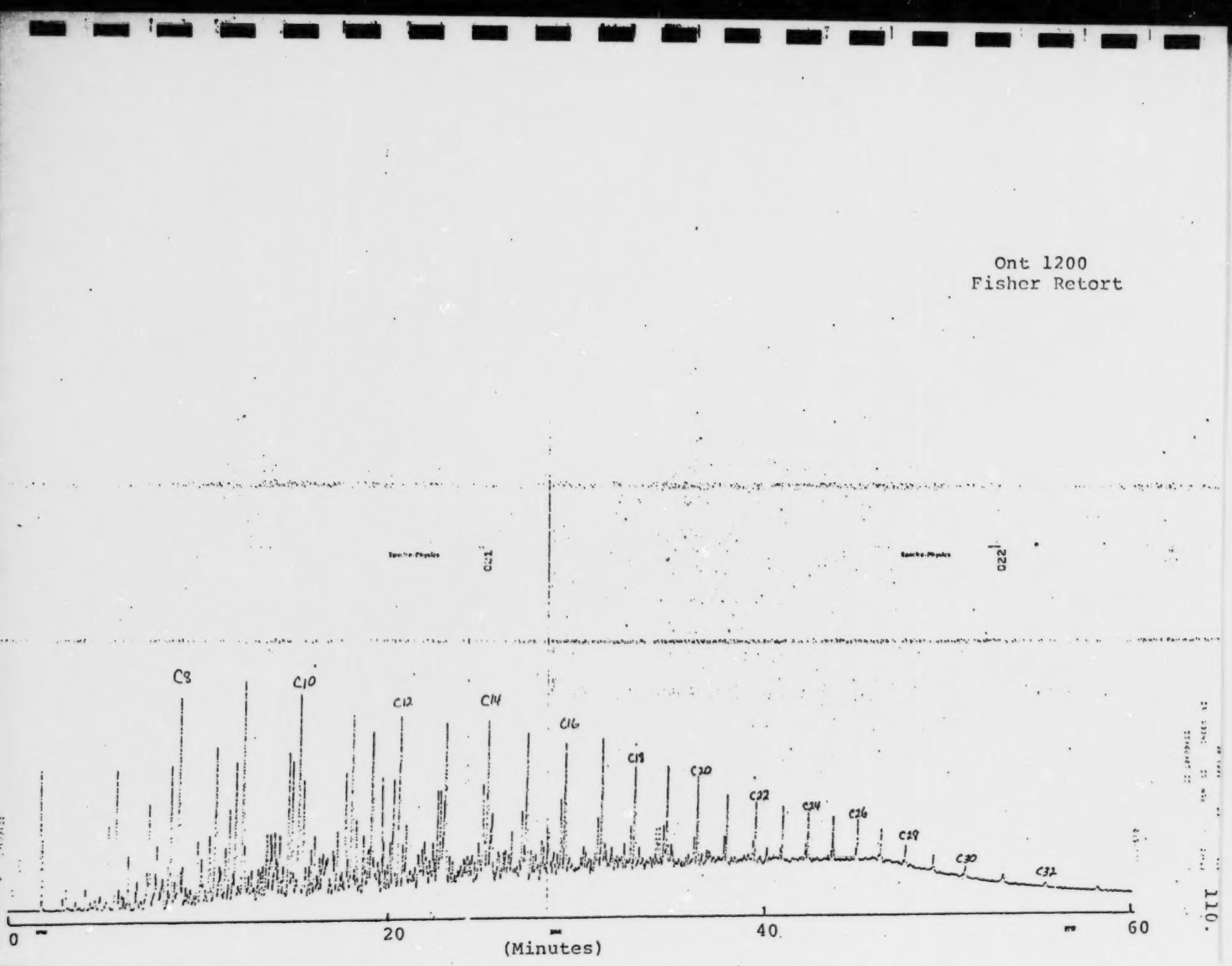
N.B. #16
Nitrogen Retort

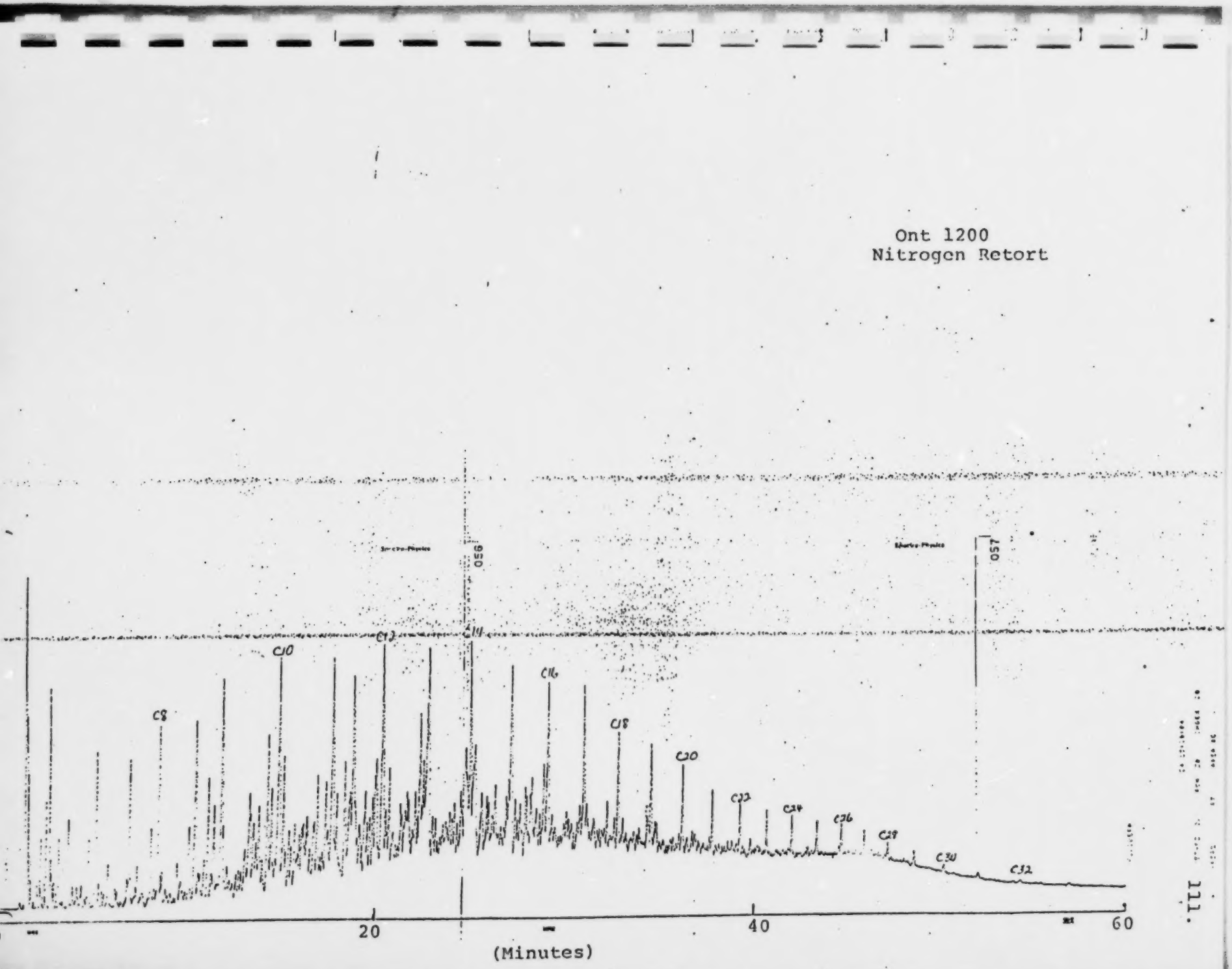


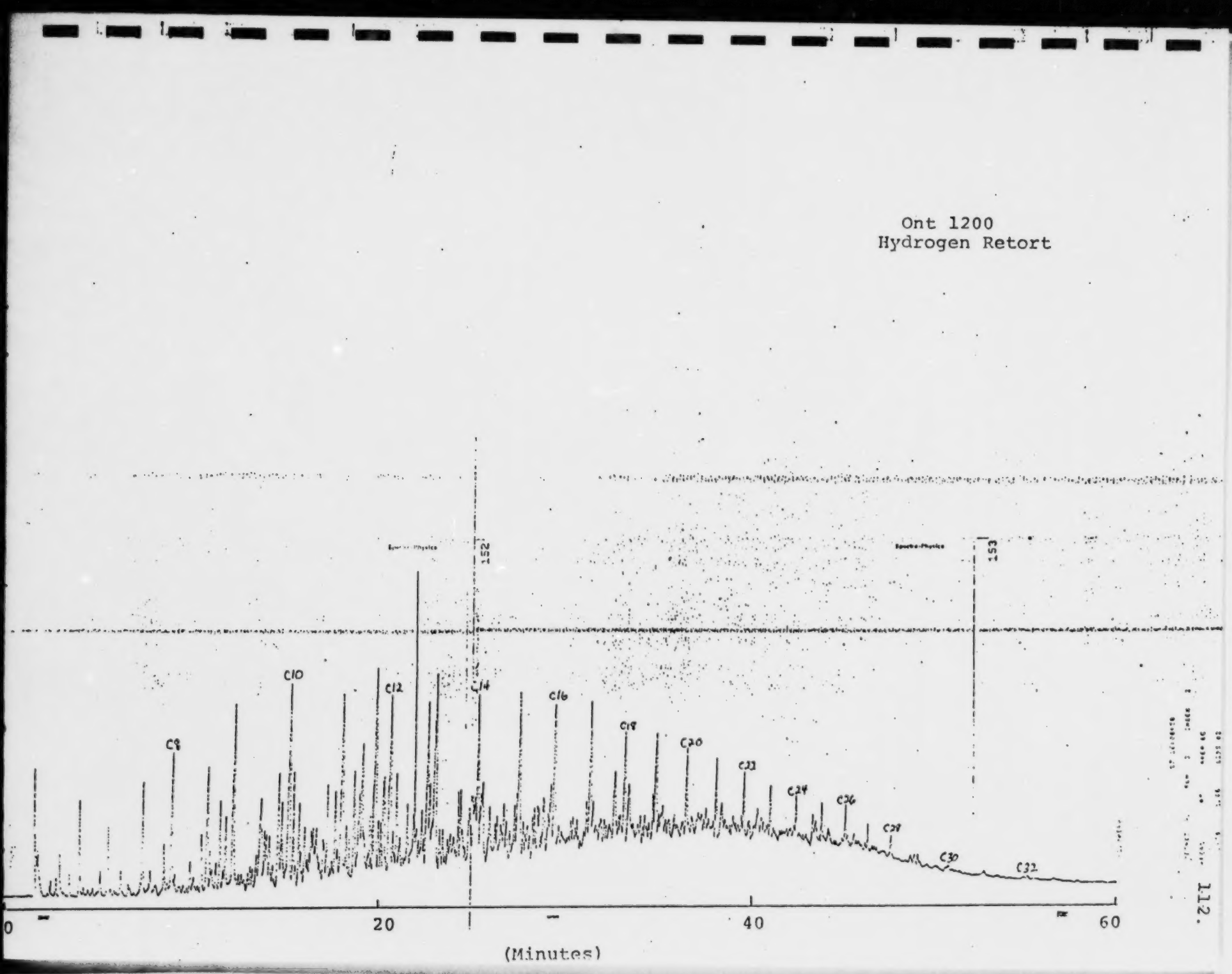

Ont 1199
Nitrogen Retort
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
20
40
60
(Minutes)

Ont 1199
Hydrogen Retort

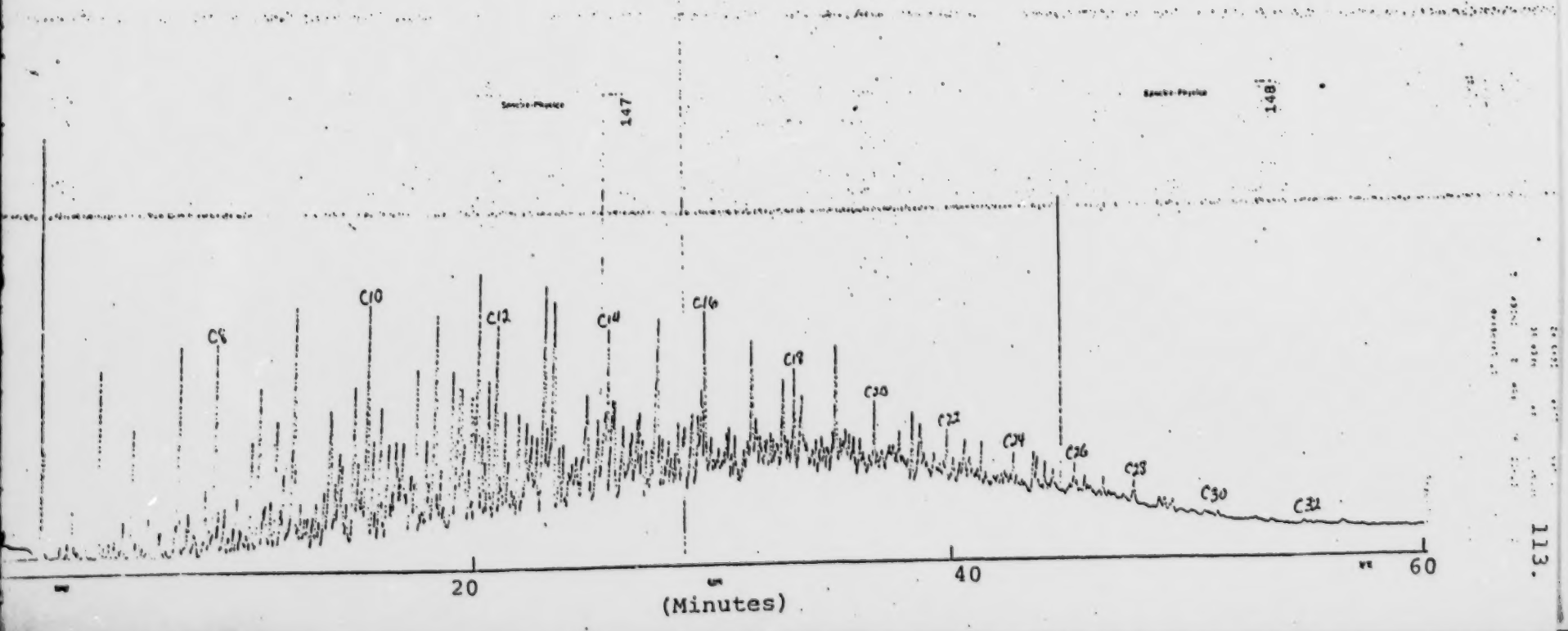



Ont 1200
Fisher Retort
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
0
20
40
60
(Minutes)
110.

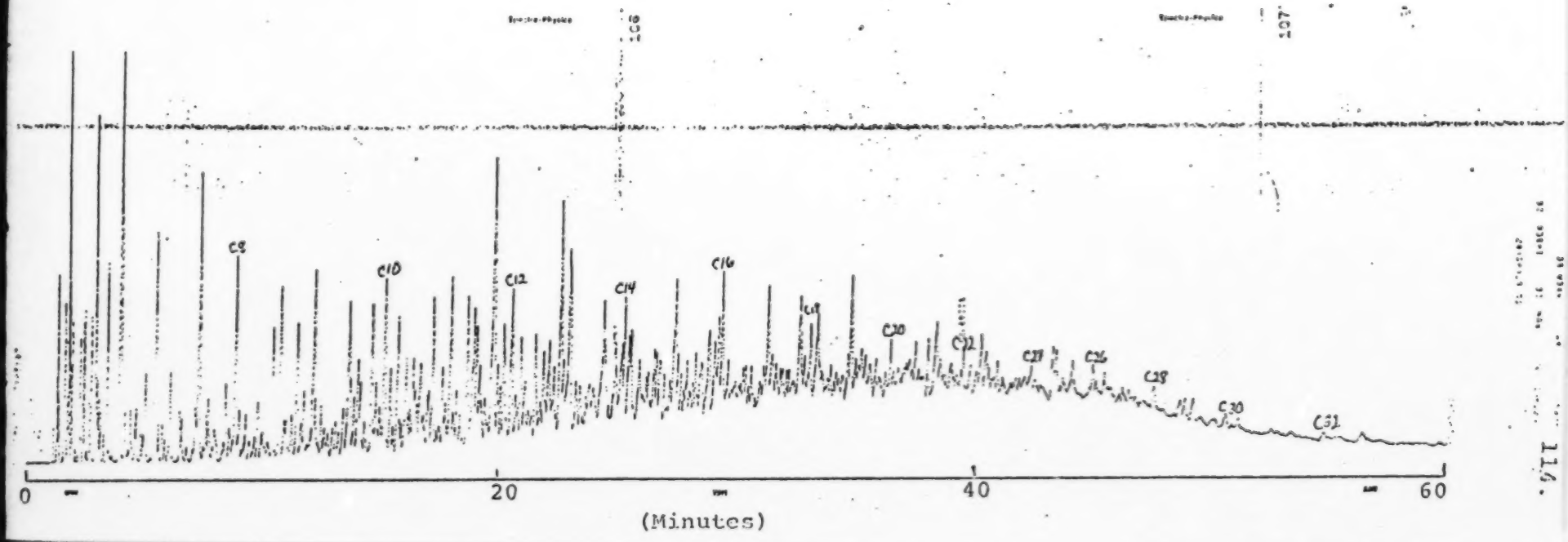

Ont 1200
Nitrogen Retort
C8
C10
C12
C16
C18
C20
C22
C24
C26
C28
C30
C32
20
40
60
(Minutes)


Ont 1200
Hydrogen Retort
152
153
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
0
20
40
60
(Minutes)

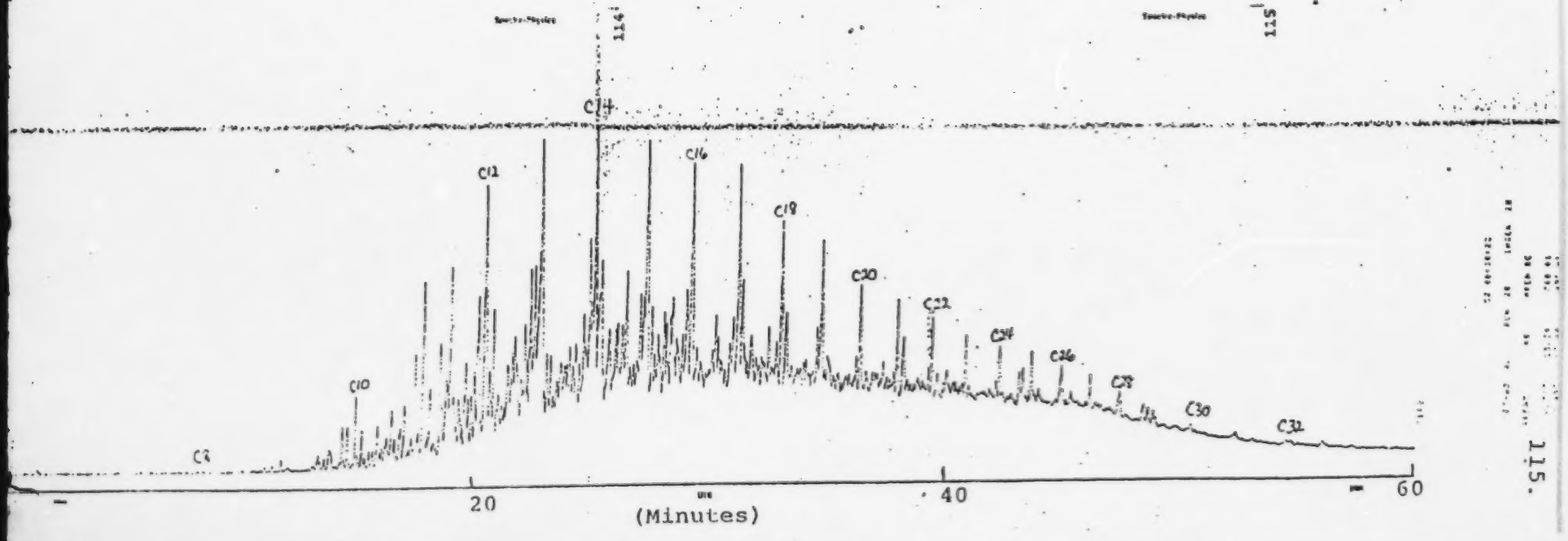
Ont 1201
Hydrogen Retort

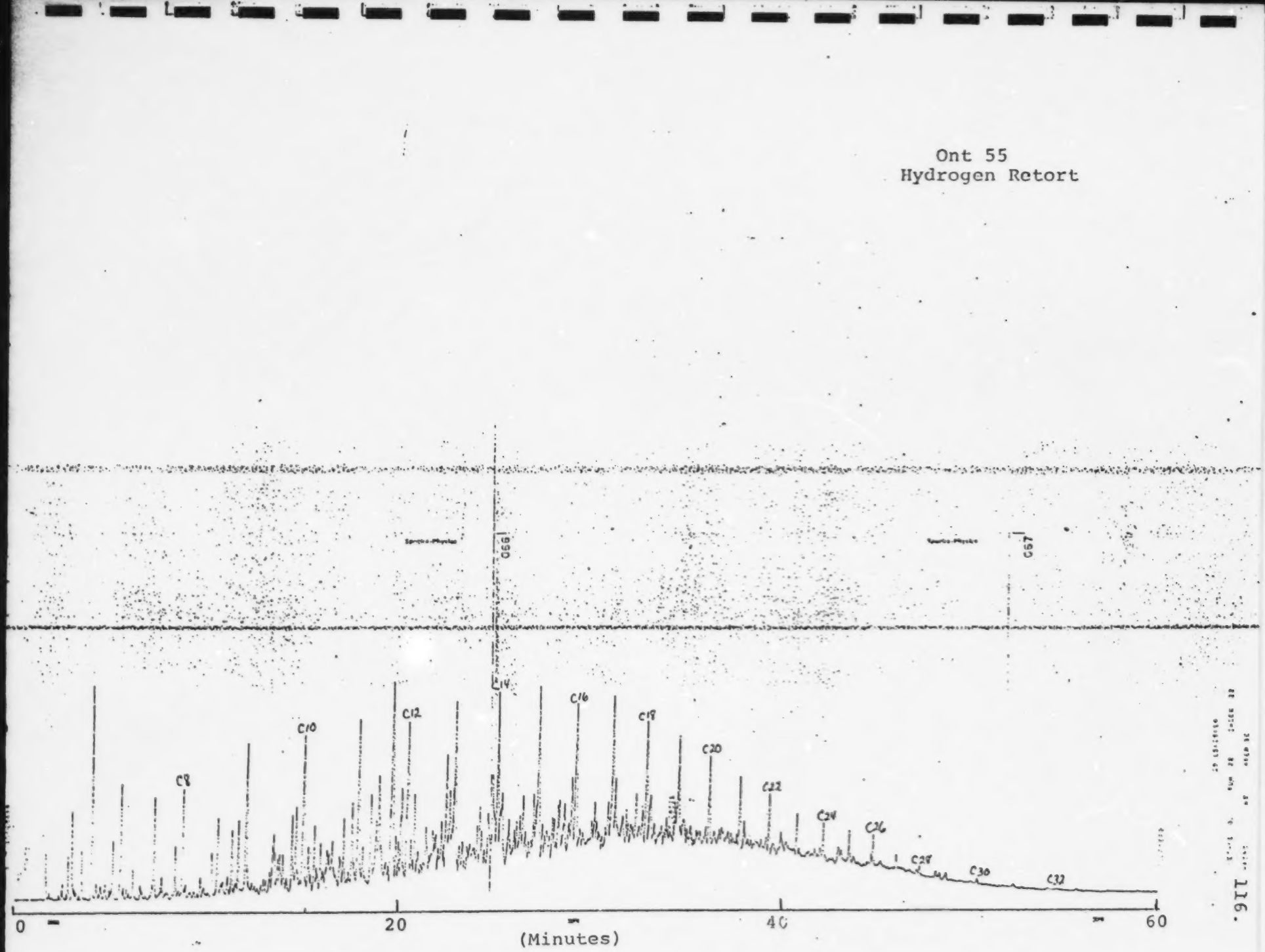


Ont 1201
Hydrogen Retort

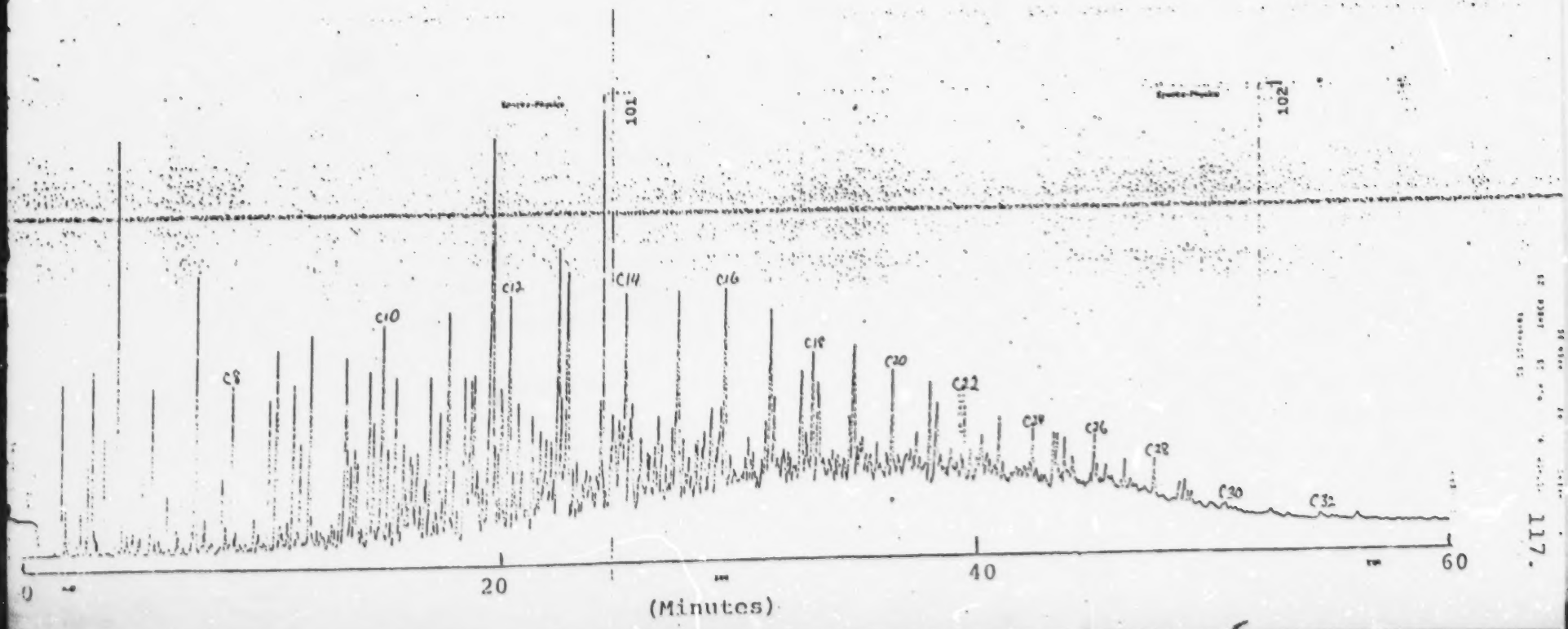


Ont 55
Nitrogen Retort

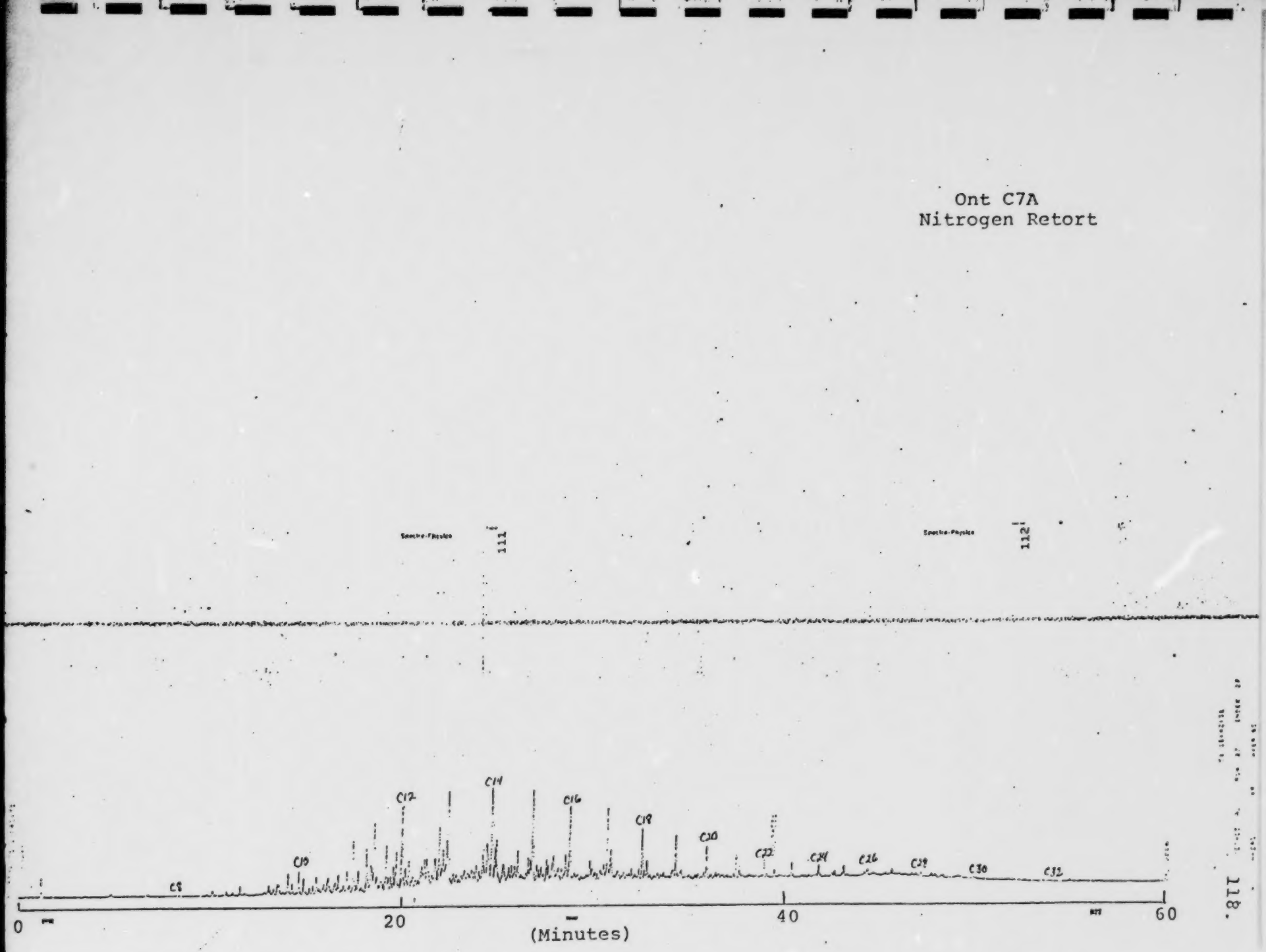



Ont 55
Hydrogen Retort
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
0
20
40
60
(Minutes)
116.

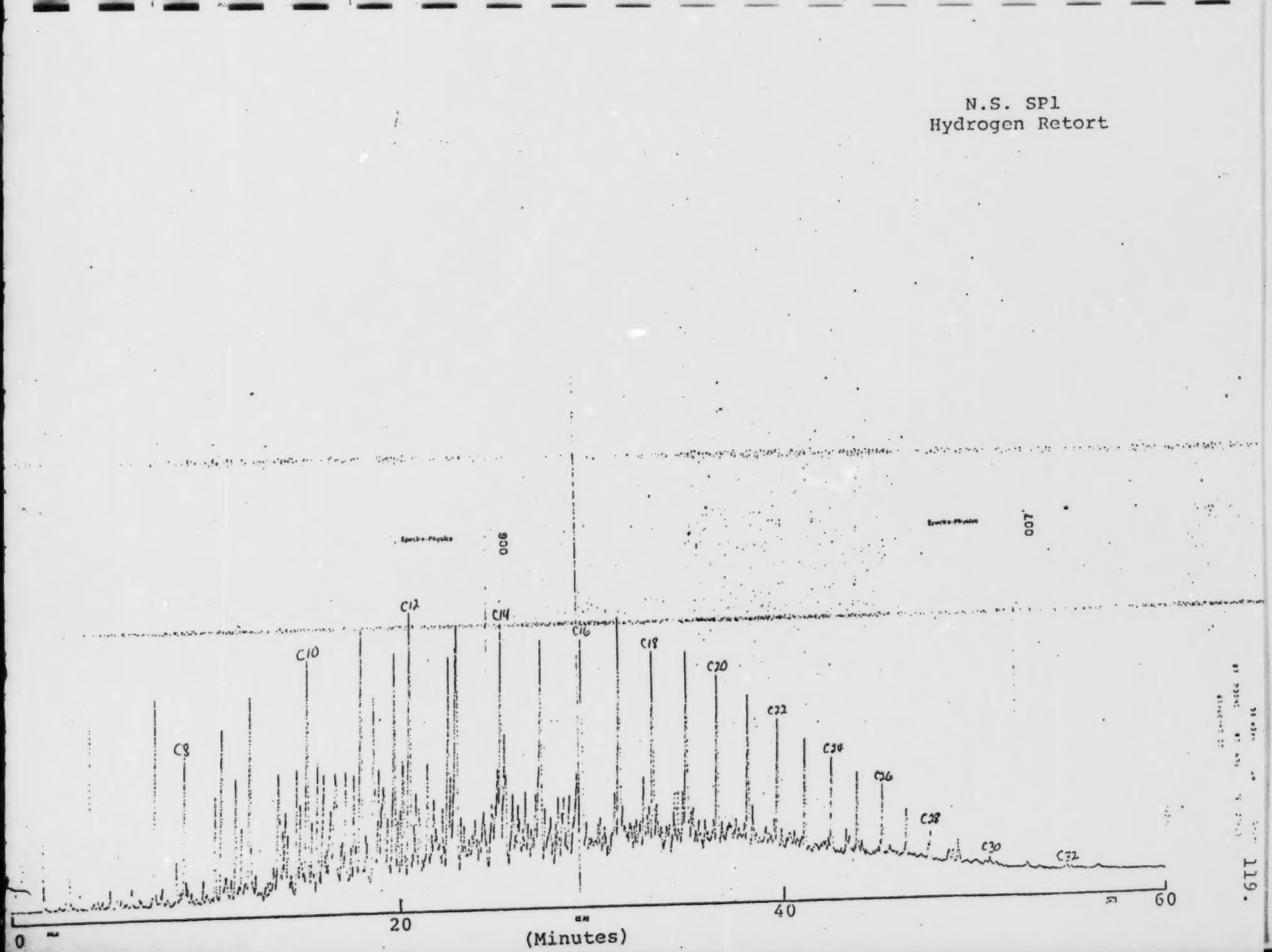
Ont C7A
Hydrogen Retort



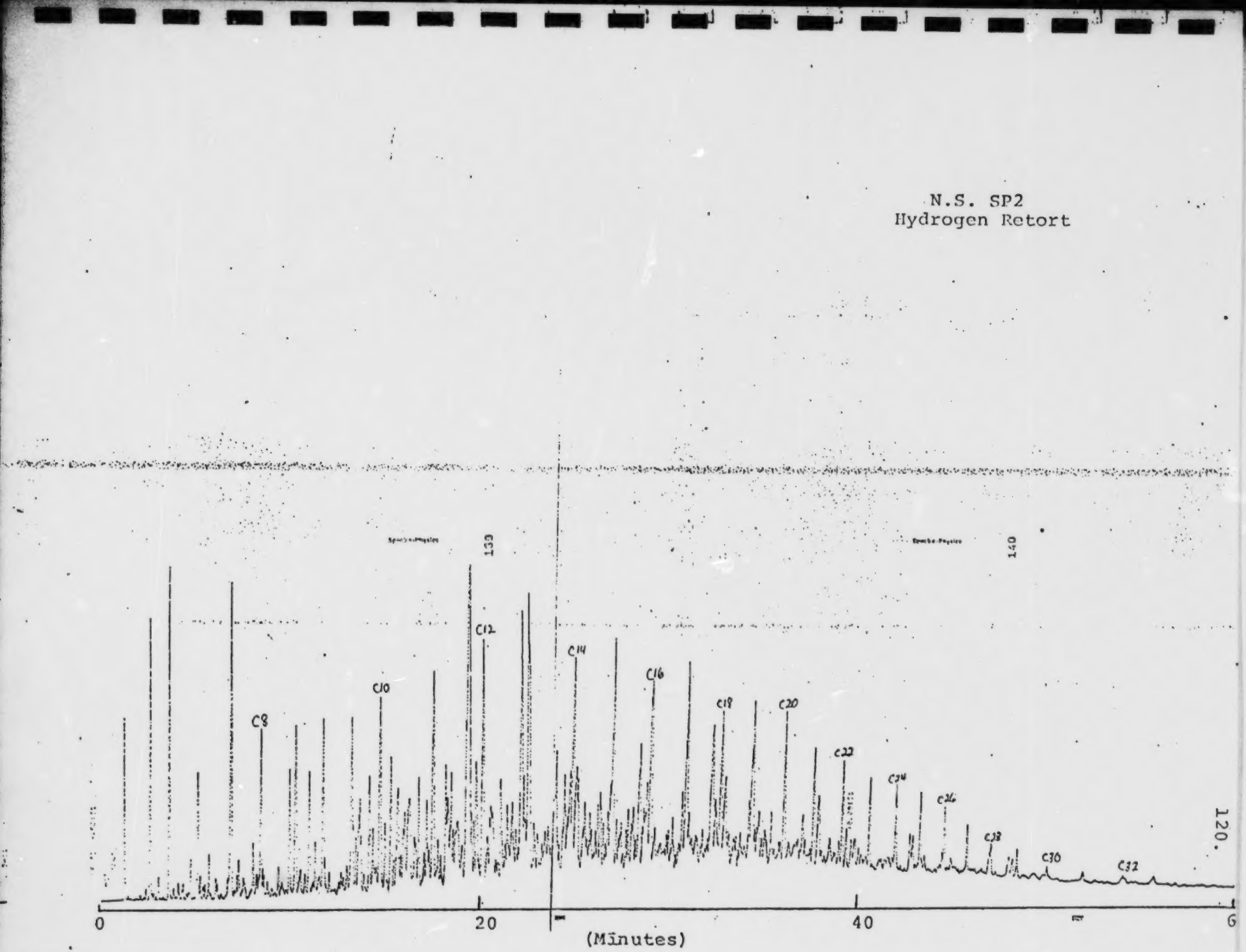
Ont C7A
Nitrogen Retort



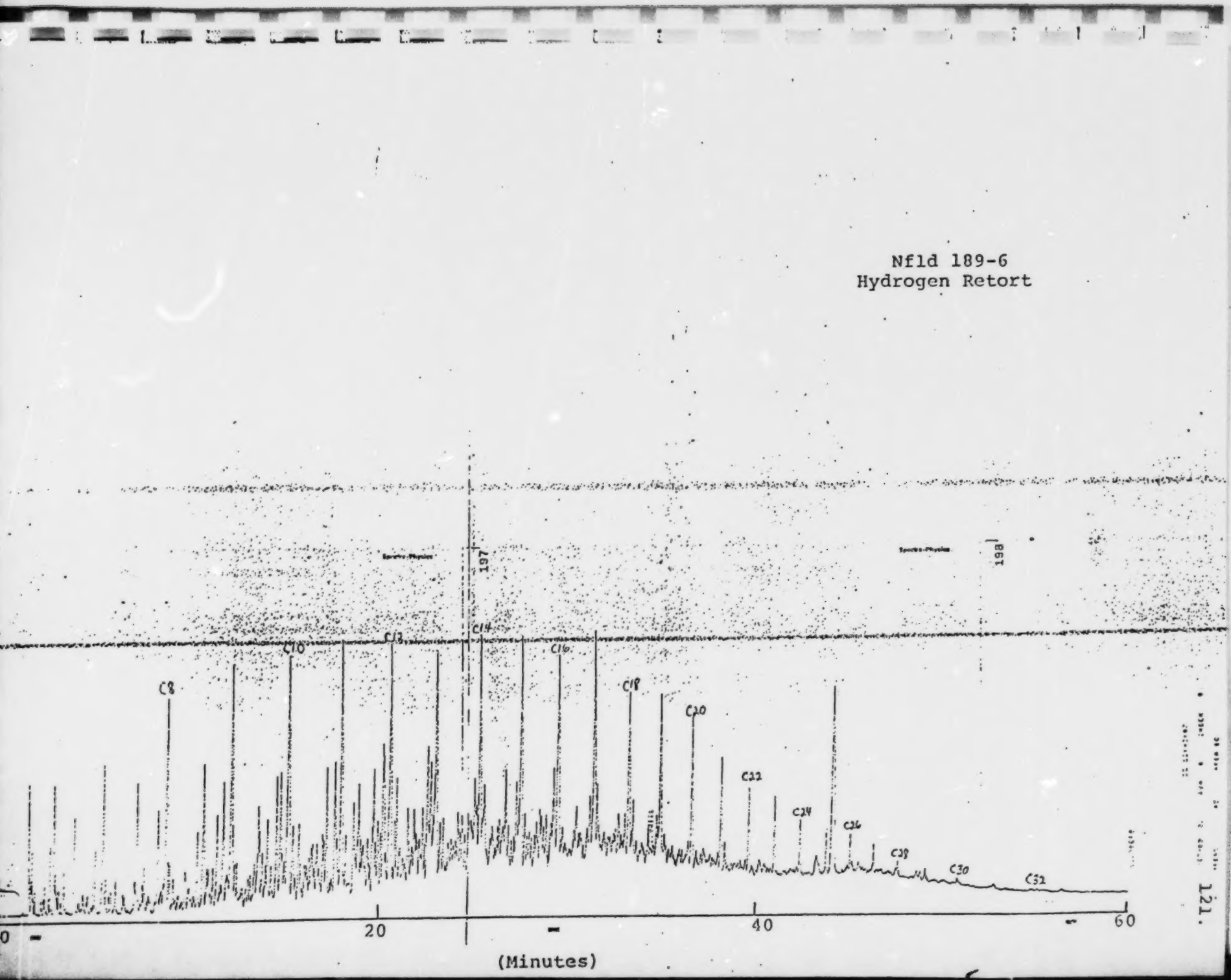
N.S. SP1
Hydrogen Retort

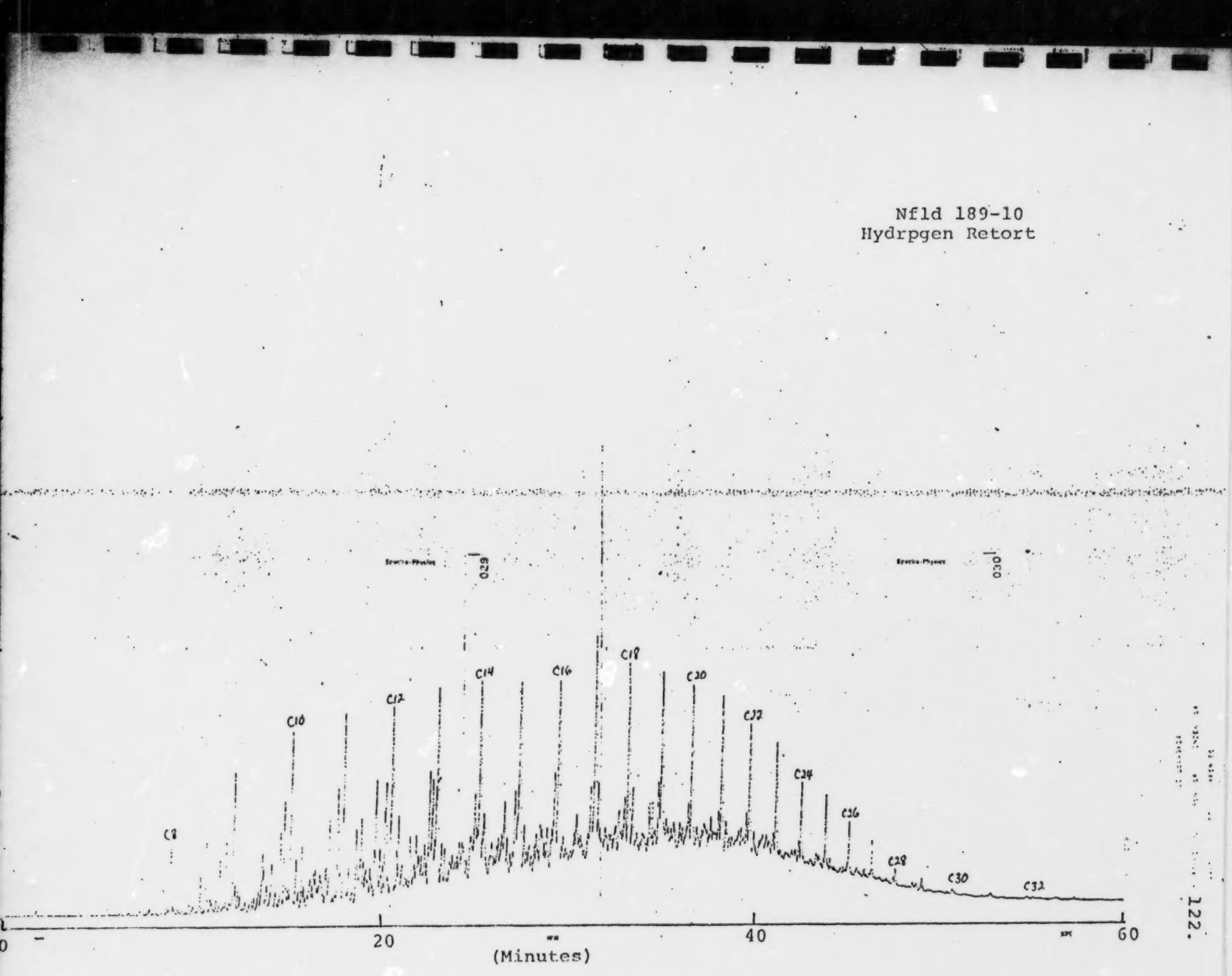


N.S. SP2
Hydrogen Retort

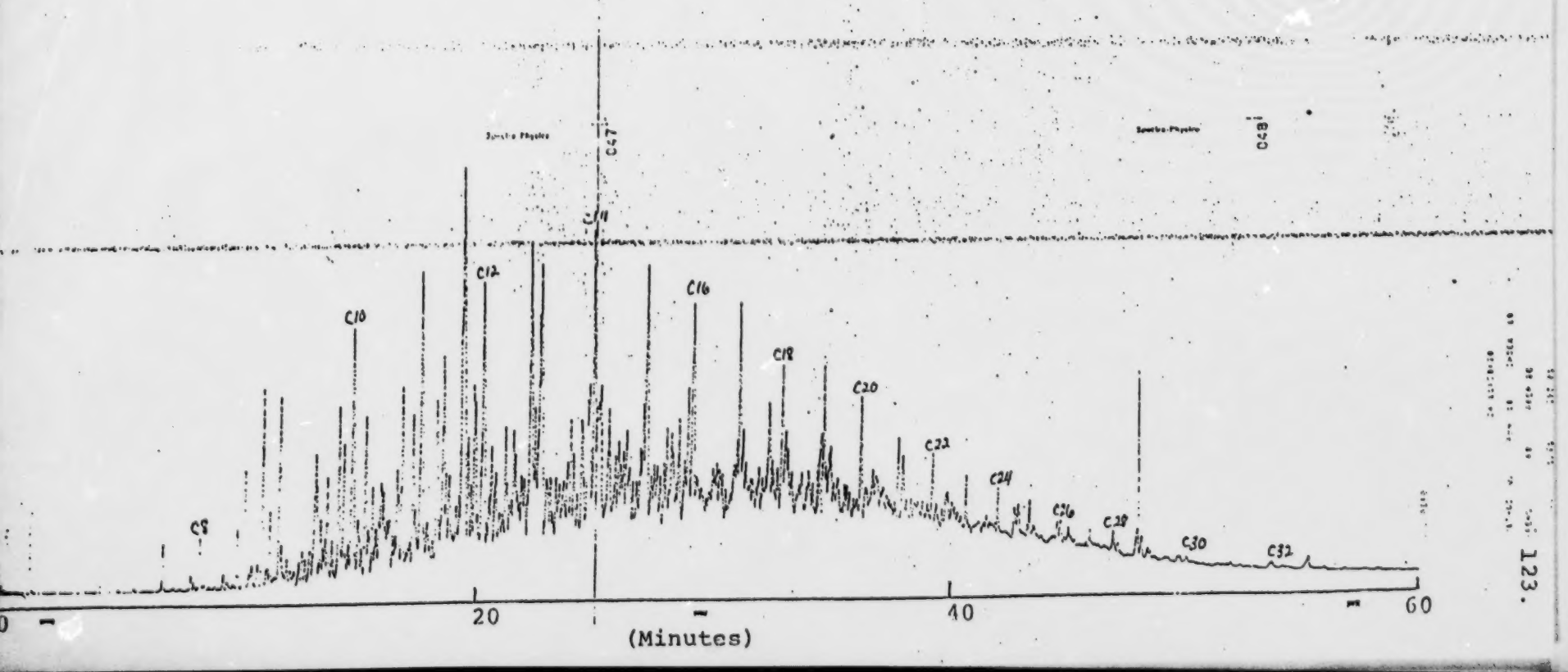


Nfld 189-6
Hydrogen Retort

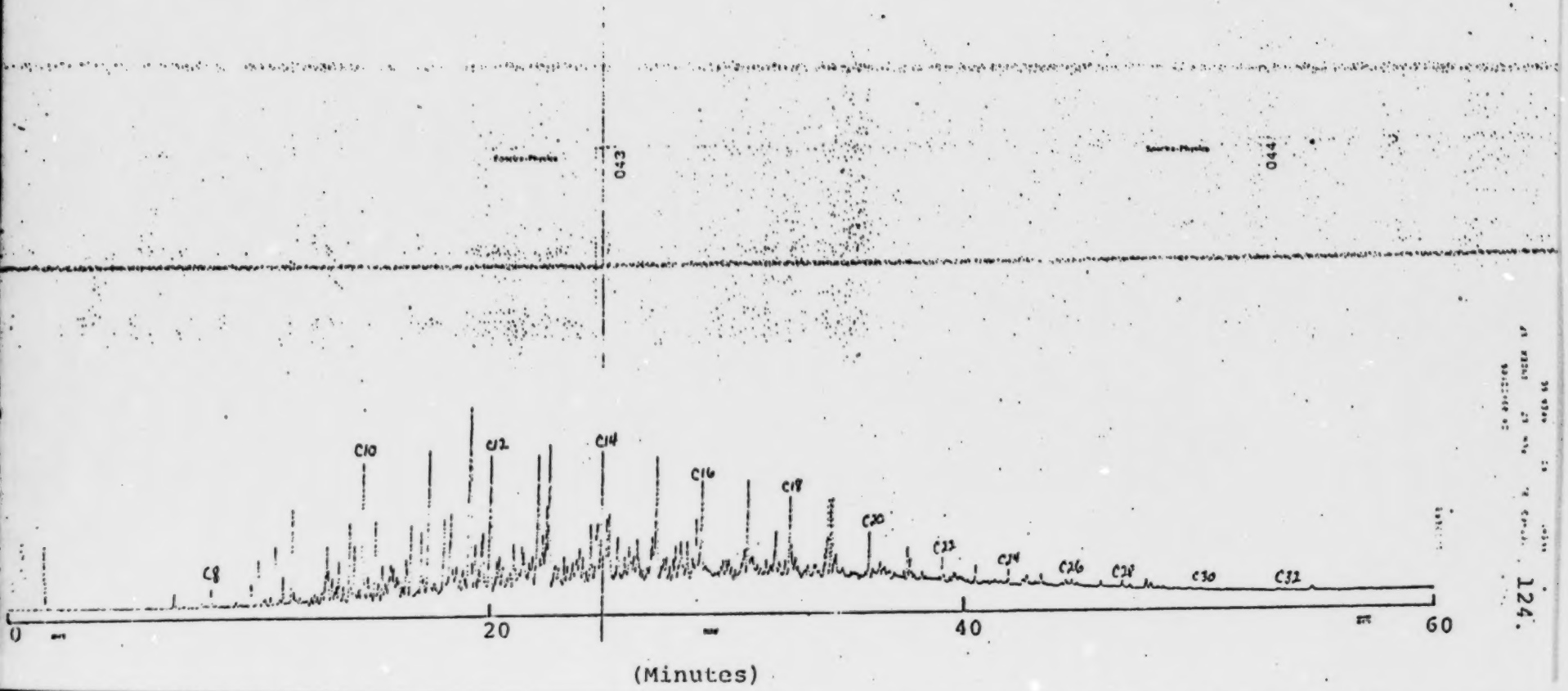



Nfld 189-10
Hydrpgen Retort
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
20
40
60
(Minutes)

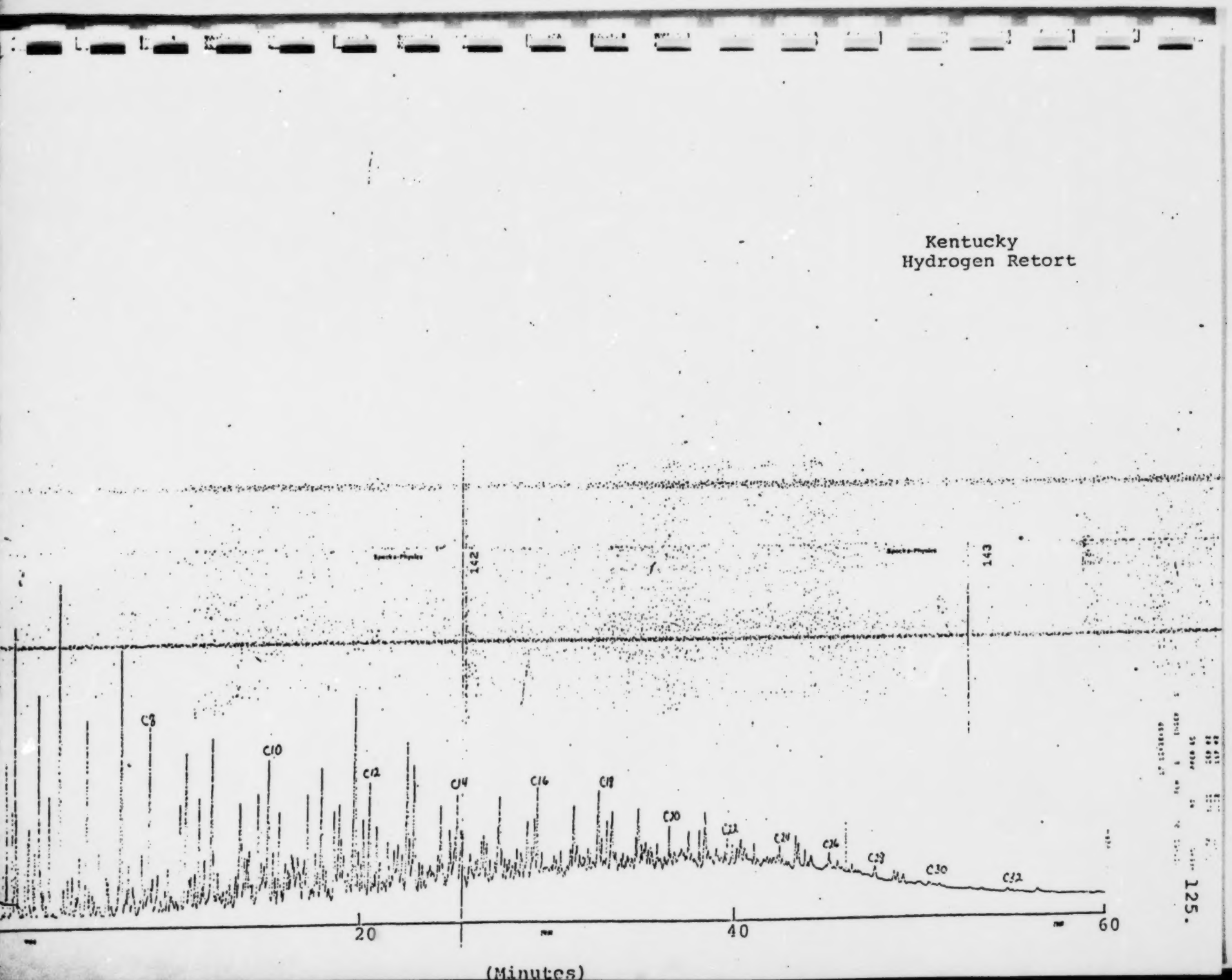
B.C.
Hydrogen Retort



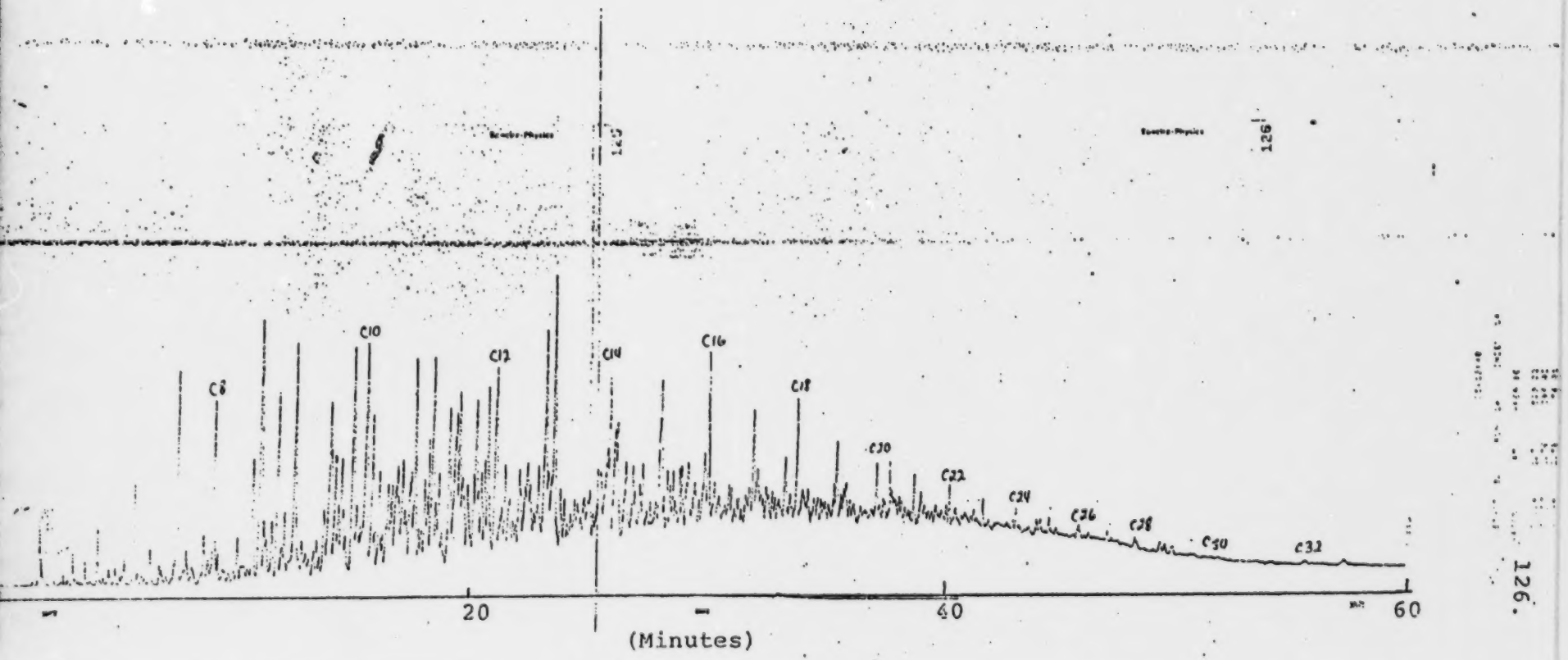
B.C.
Hydrogen Retort



Kentucky
Hydrogen Retort



Kentucky
Nitrogen Retort



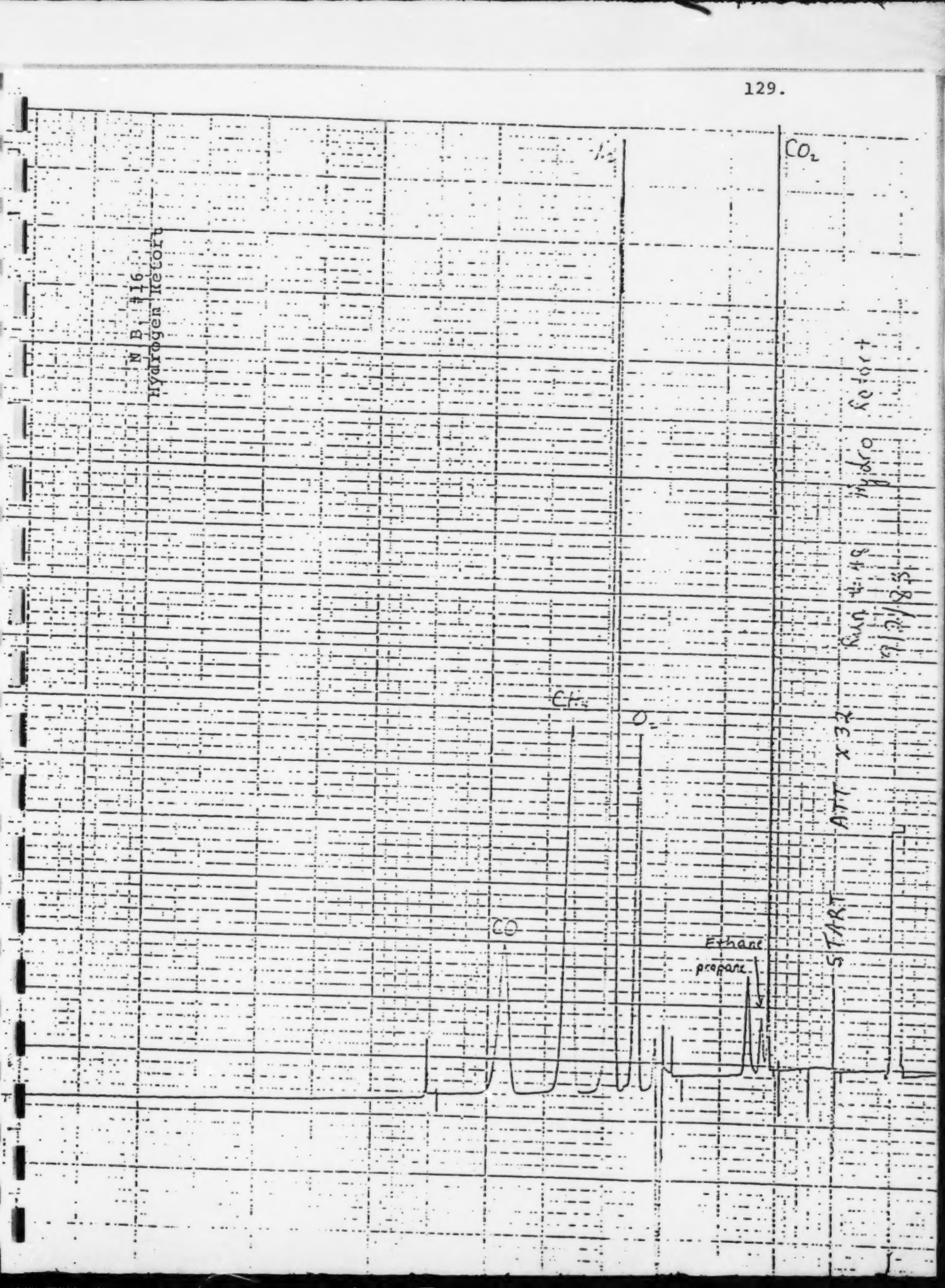
APPENDIX 9.5

SAMPLE GAS CHROMATOGRAMS OF EFFLUENT GASSES

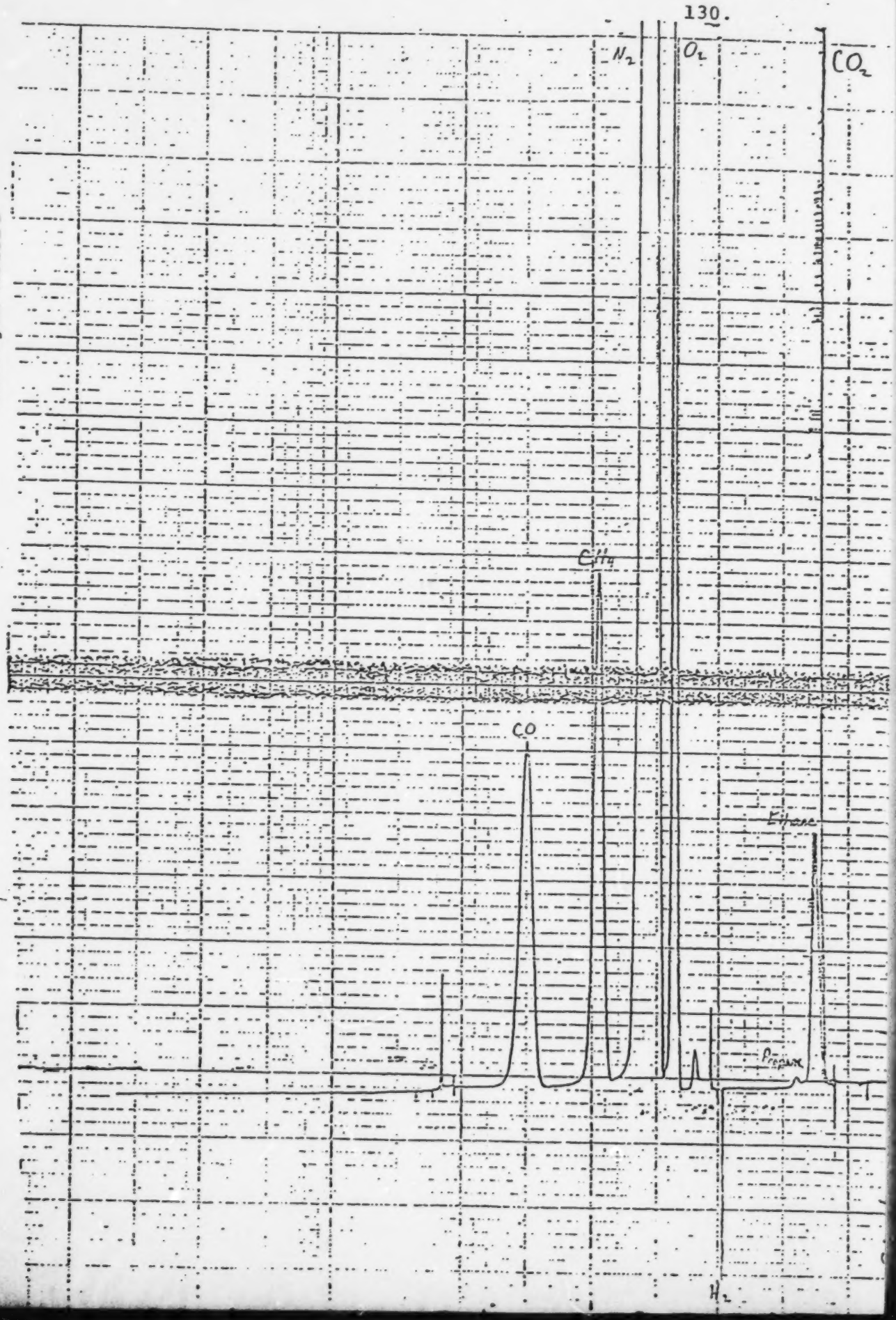
9.5 GAS CHROMATOGRAPHY OF EFFLUENT GASSES

The effluent gases were analysed using a Carle Model III Analytical Gas Chromatograph with a thermalconductivity detector and thermistor elements. The following conditions were used:

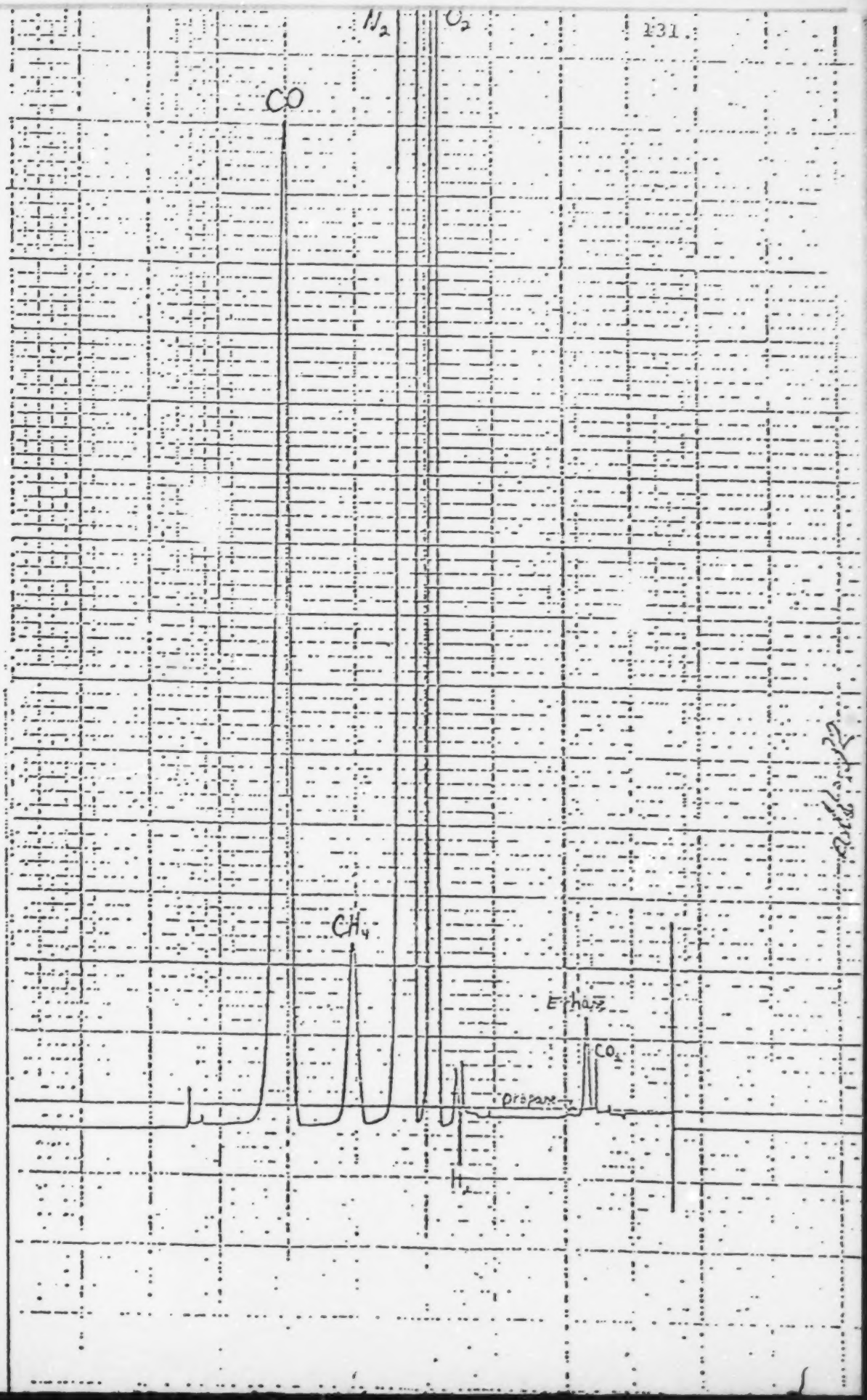
Sample size	-	1.0 ml
Oven temperature	-	98°C
Carrier gas	-	He, 42 psi, 31 ml/min
Senstitivity	-	Standard
Column 1	-	8' x 1/8" Porapak/Carbowax
Column 2	-	6' x 1/8" Molecular Sieve 5A, 42 - 60 mesh

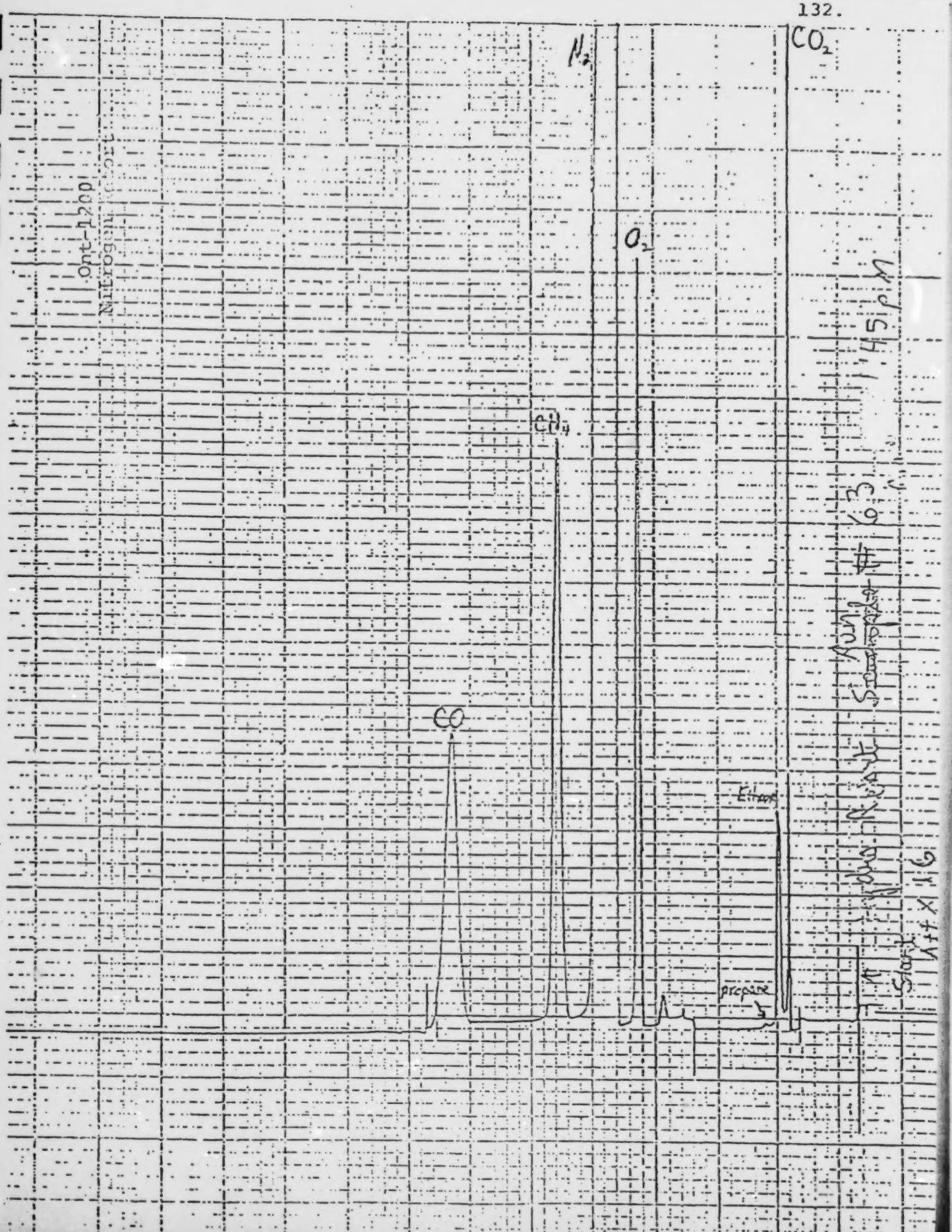

N B #16
Hydrogen Retort
CO
Ethane
propane
START

N.B. #16
Nitrogen Retort

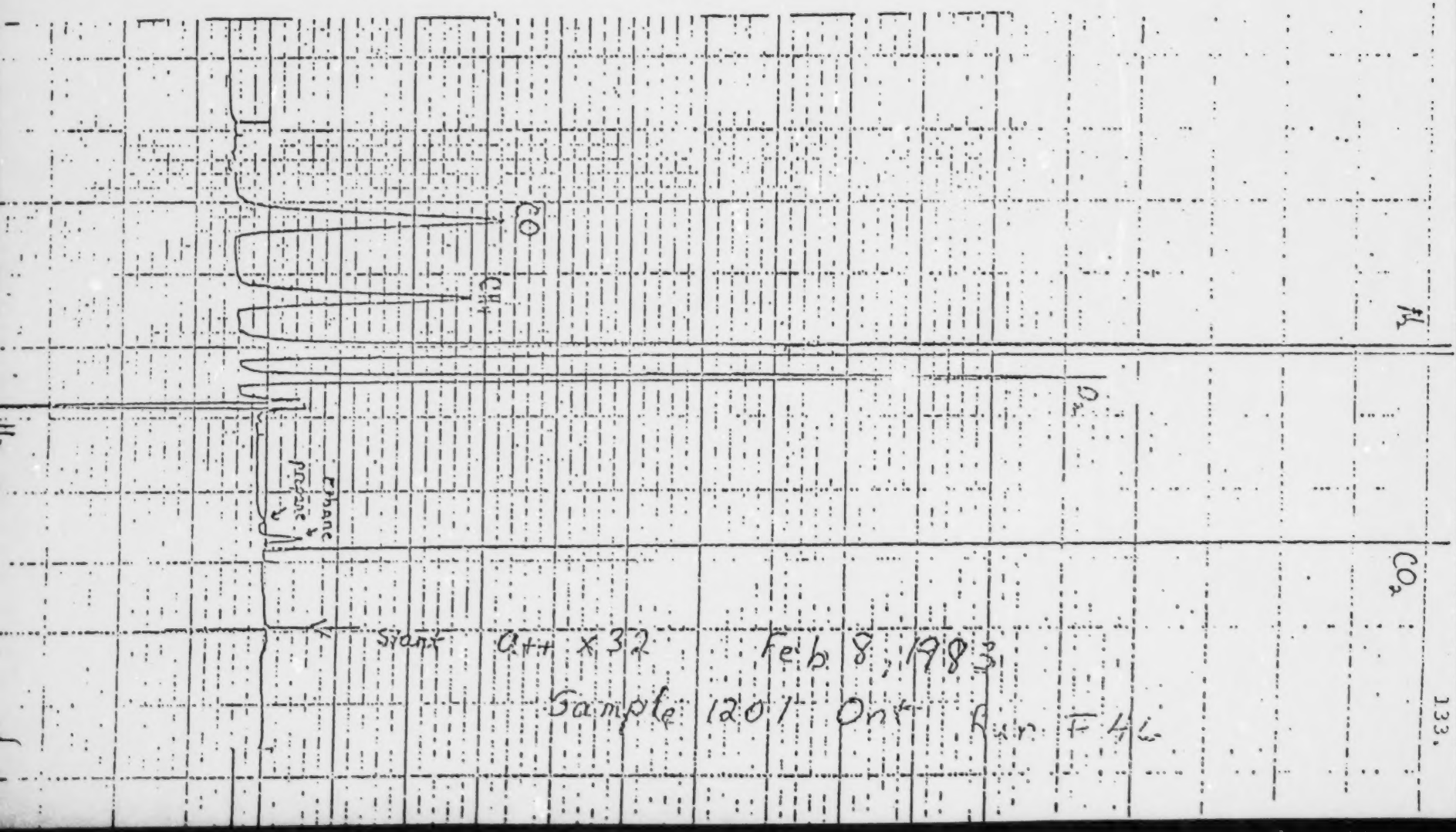


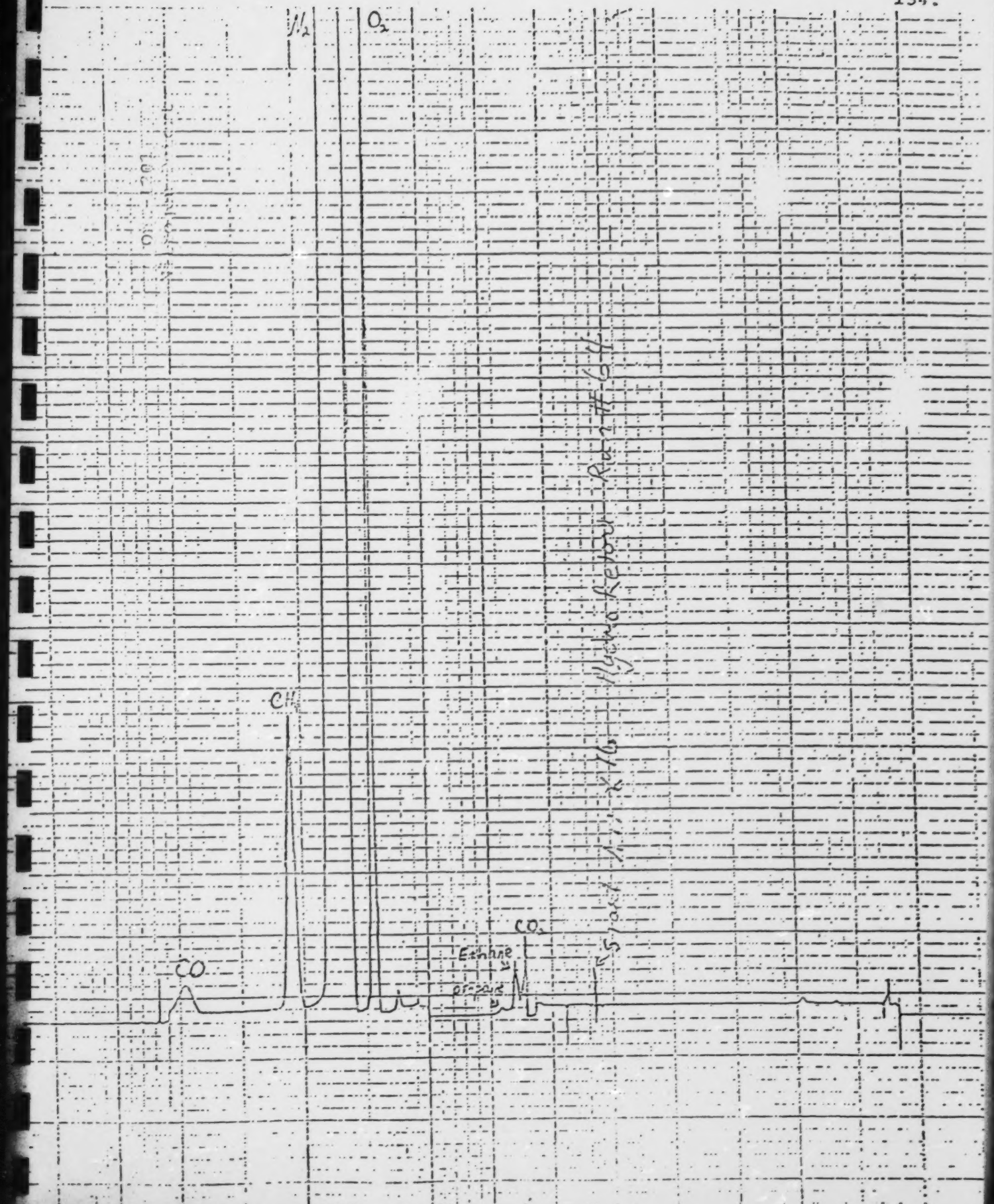
Ont-1200
Hydrogen Retort




H_2
CO_2
O_2
CH_4
CO
Ethane
propane

Ont-1201
Hydrogen Retort




H2
O2
CH4
CO
CO2
Ethane
Propane